Monitored Natural Attenuation (MNA):

Assessment, Prediction, and Verification

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U.S. Geological Survey

MNA Outline

- Background
- Assessment
- Prediction/Verification
- References
- Points of Contact

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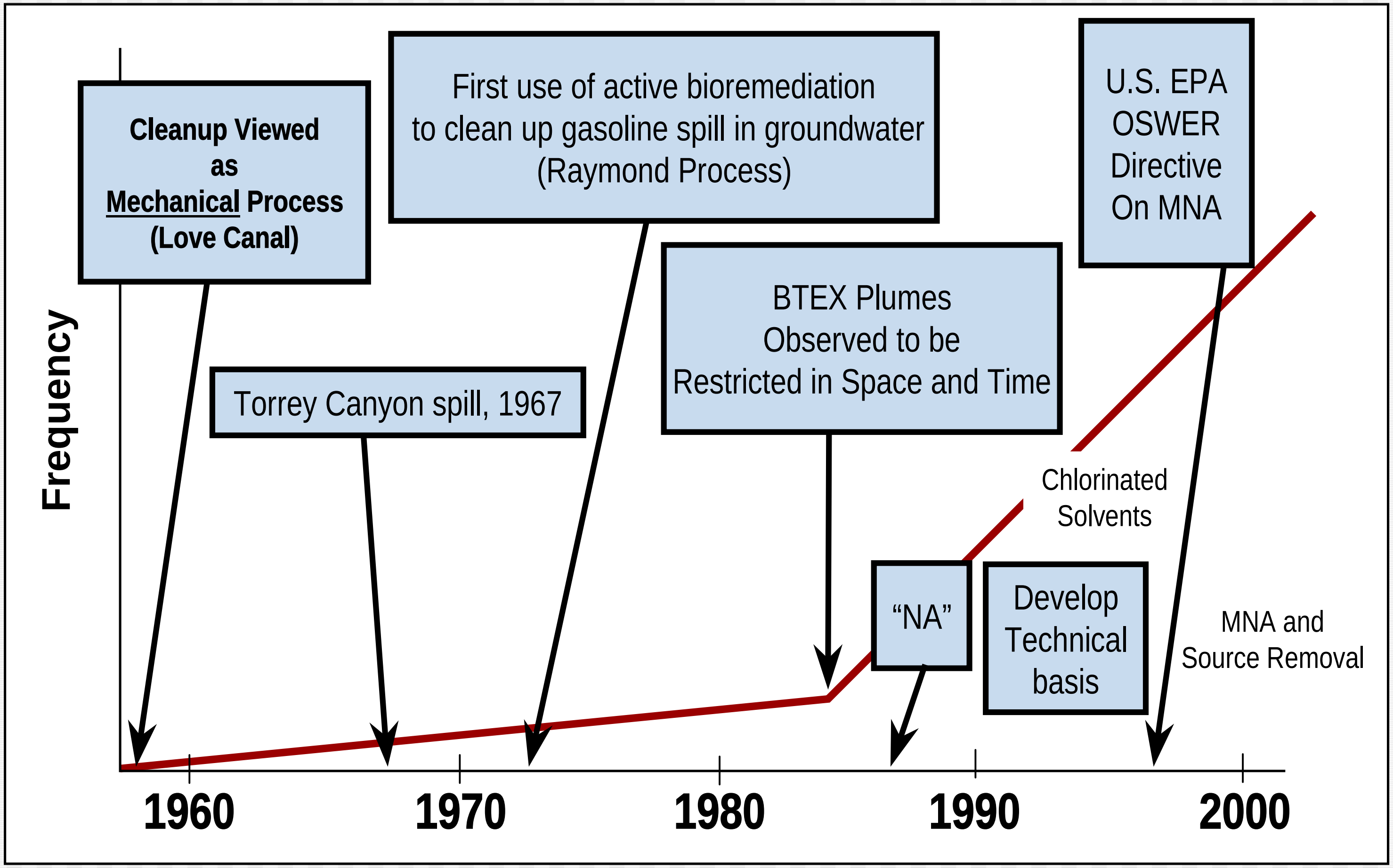
MNA is a.k.a.:

- Intrinsic bioremediation
- "Natural attenuation" (circa 1987)
- Natural bioremediation
- Bioreclamation

Brief History of MNA



1997 EPA OSWER Directive:

Natural Attenuation Processes include "physical, biological, and chemical processes". These are:

- Physical = dispersion (D), advection (v)
- Biological = reduction, oxidation (k)
- Chemical = sorption (S)

…Not just biological!

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Site Assessment
Should Consider Multiple Lines of Evidence

- Redox Conditions
  - Presently observed conditions
- Distribution of Daughter Products
  - Record of past conditions
- Hydrologic Framework
  - Prediction of future conditions

The efficiency of natural attenuation depends on the balance between these forces:

- Dispersive capacity of the aquifer
- Velocity of groundwater

] "Driving Forces"

- Sorptive capacity of aquifer
- Rates of biodegradation

] "Resisting Forces"

How is this quantified for use at contaminated sites?

How can we take all of these processes into account, simultaneously?

- To illustrate, let's do a visual experiment:

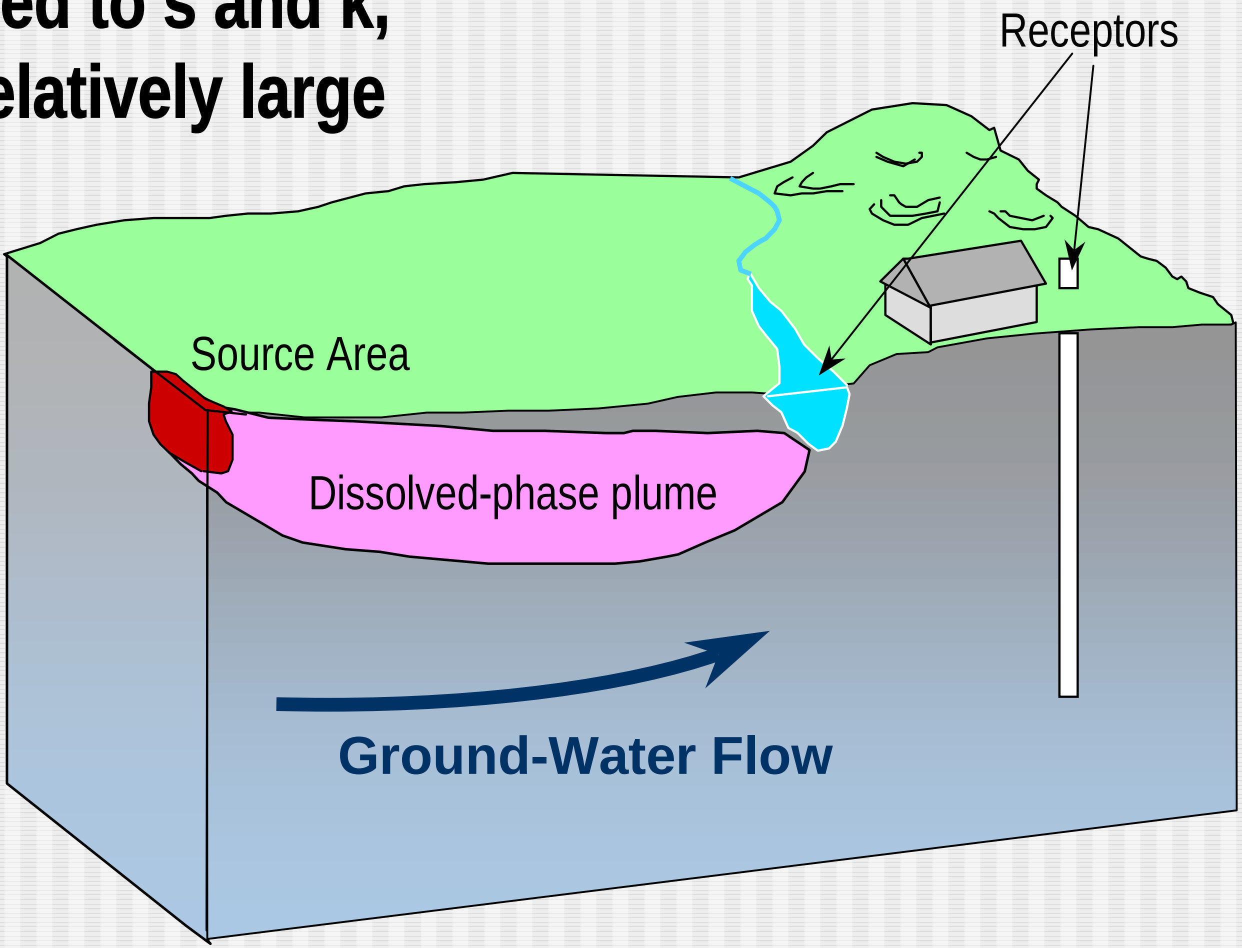
***Consider a contaminant spill that reaches the water table. The size of the contaminant plume that eventually develops is controlled by*:**

- Size of the spill (volume, source area footprint, etc.)
- Velocity of groundwater flow (v)
- Biodegradation (k)
- Sorption (S)

Principle:

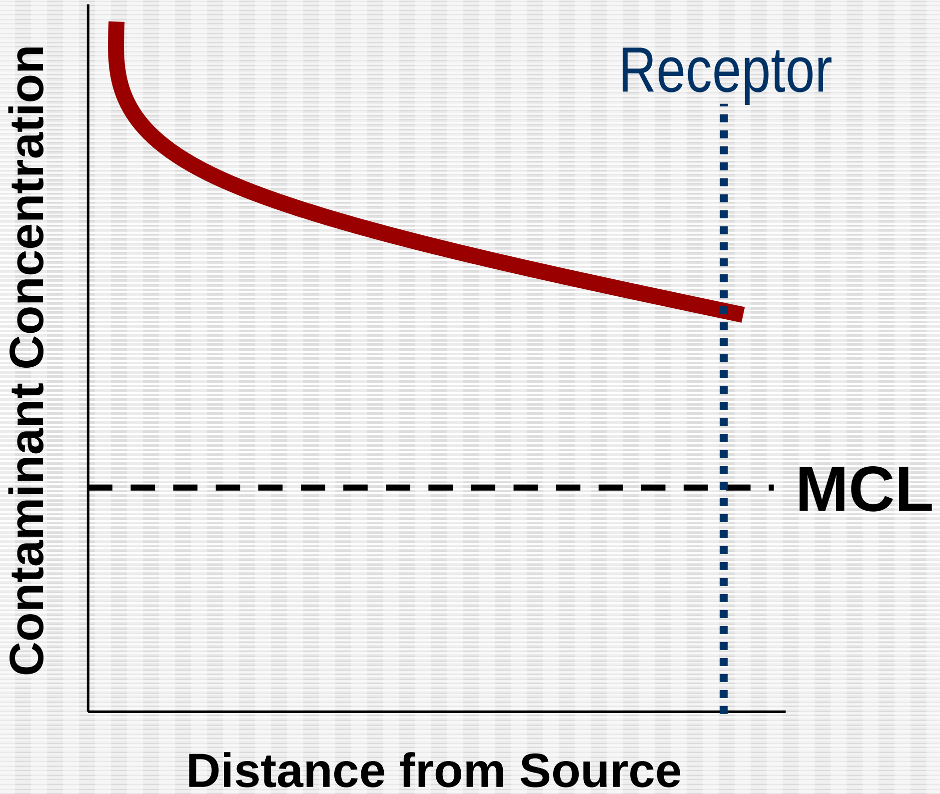
If v is large compared to s and k, the plume will be relatively large

$$v \gg k,s$$



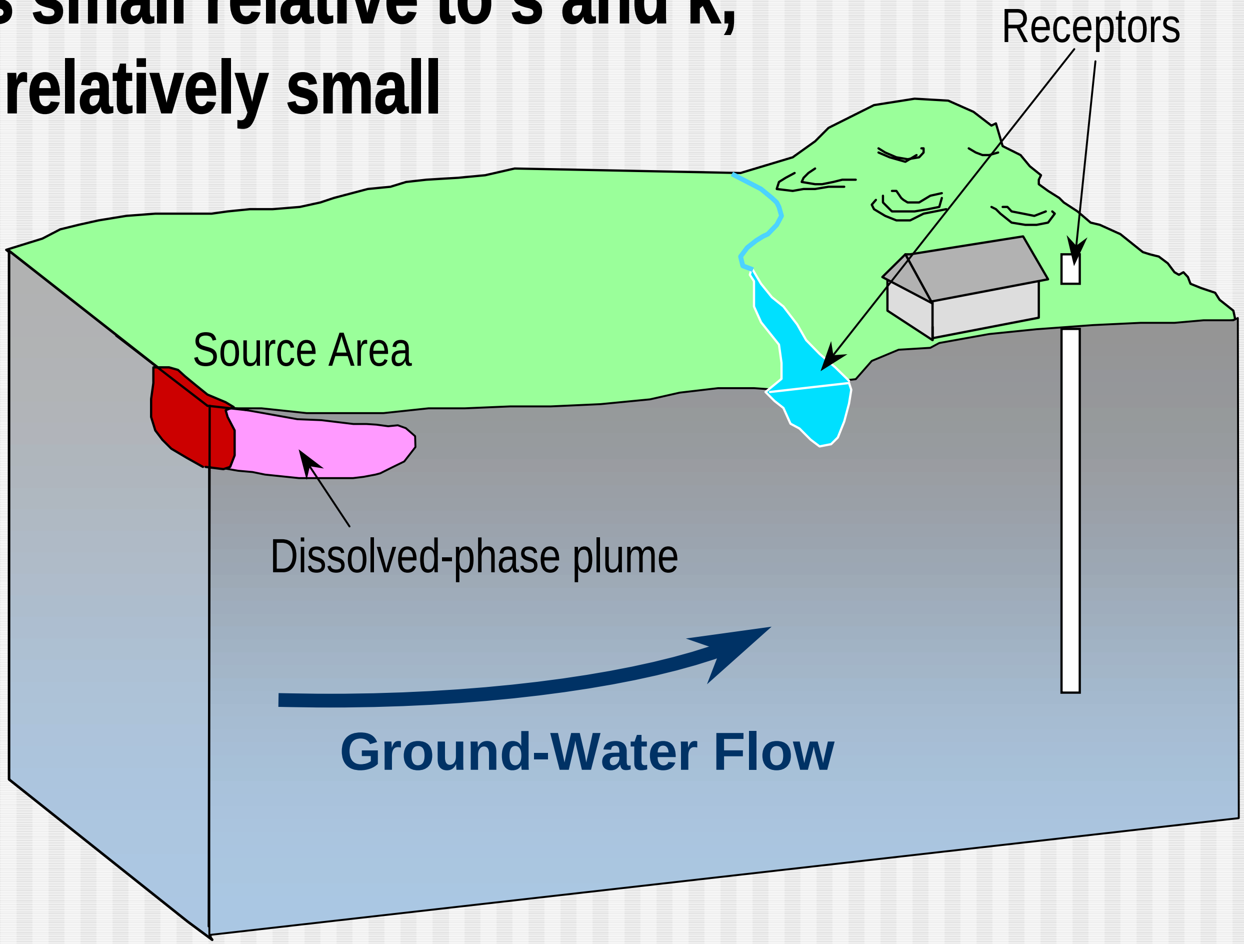
Inefficient NA =

slow decrease of contaminants away from source area



Principle:

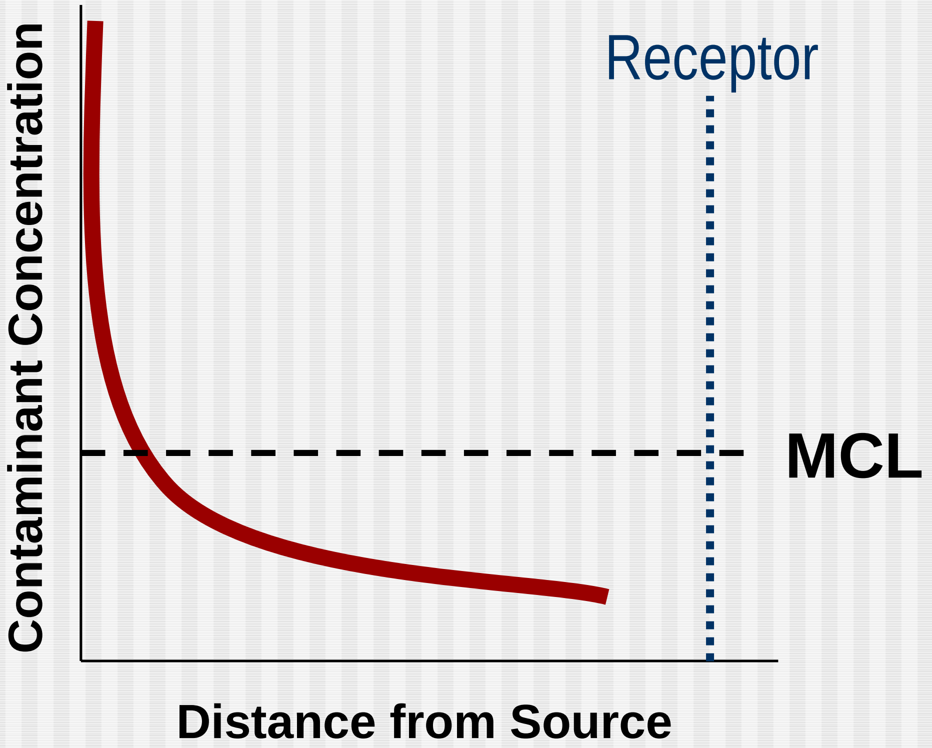
Conversely, if v is small relative to s and k, the plume will be relatively small



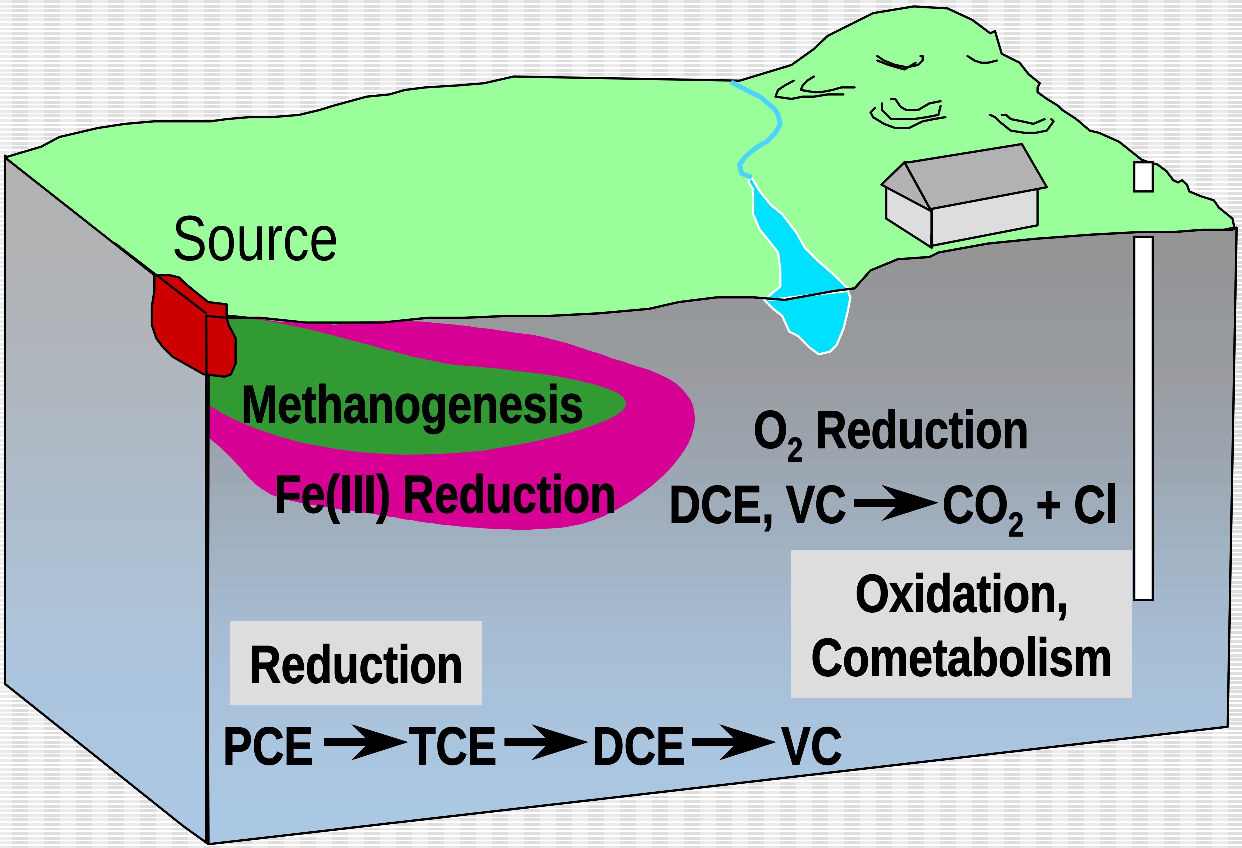
$v << k,s$

Efficient NA =

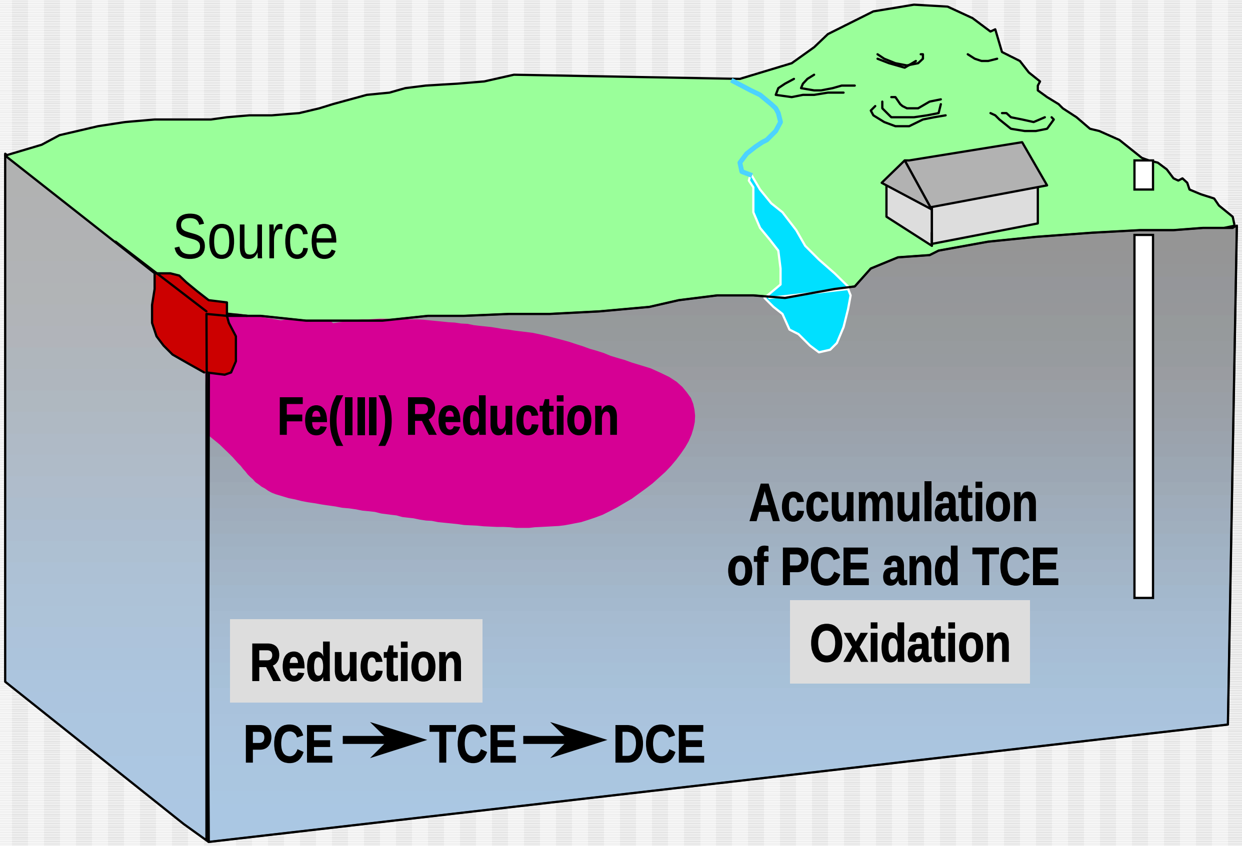
rapid decrease of contaminants away from source area



Efficient Natural Attenuation



Inefficient Natural Attenuation



Next Question:

How do you get this information (D,v) to make a decision about MNA?

- Hydrogeologic info (D, v)
- Monitoring well installation (areally, vertically)
- Water levels, flow directions, gradients
- Flowrates (K)
- Effect of these parameters on contaminant data interpretation

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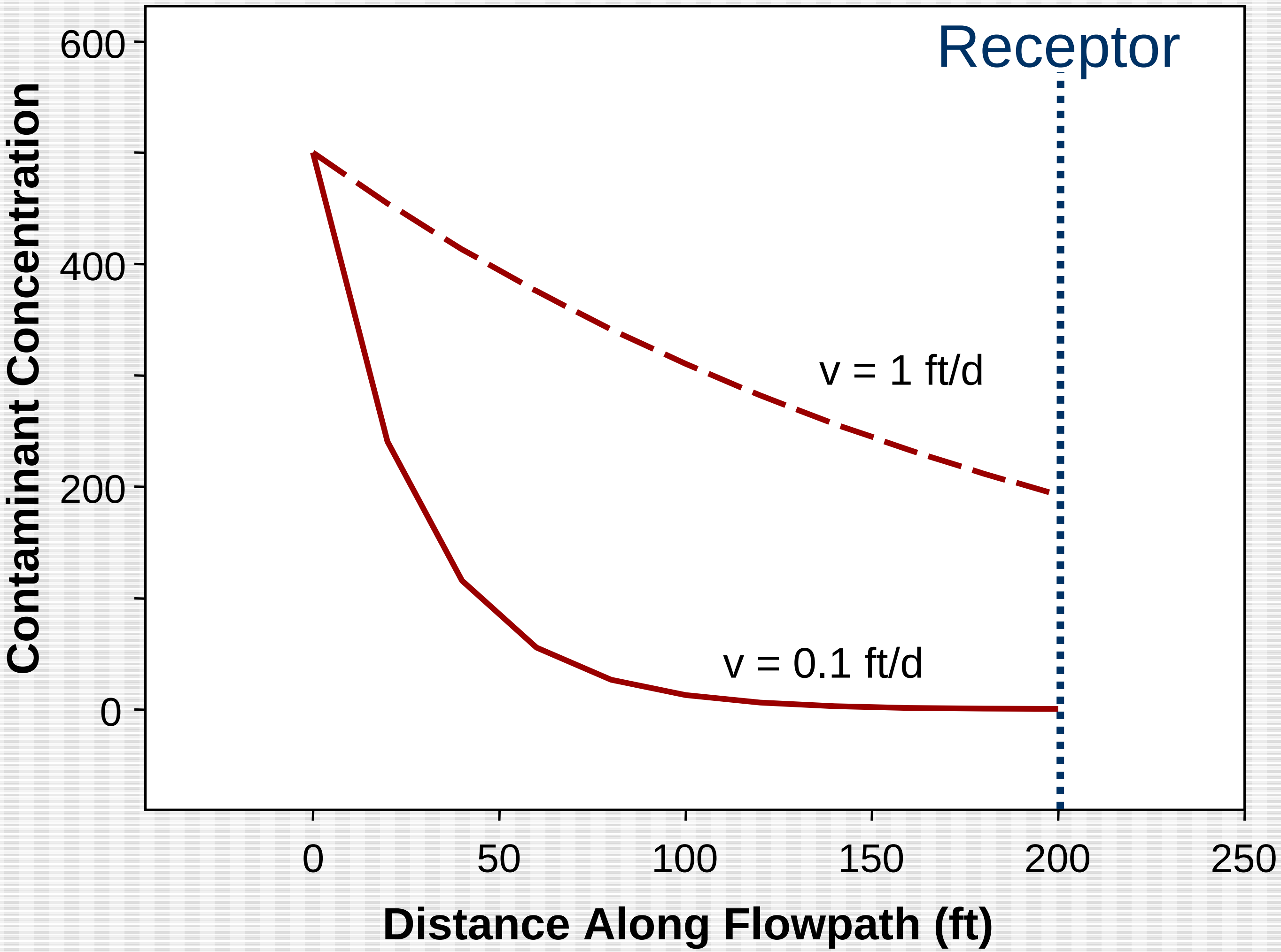
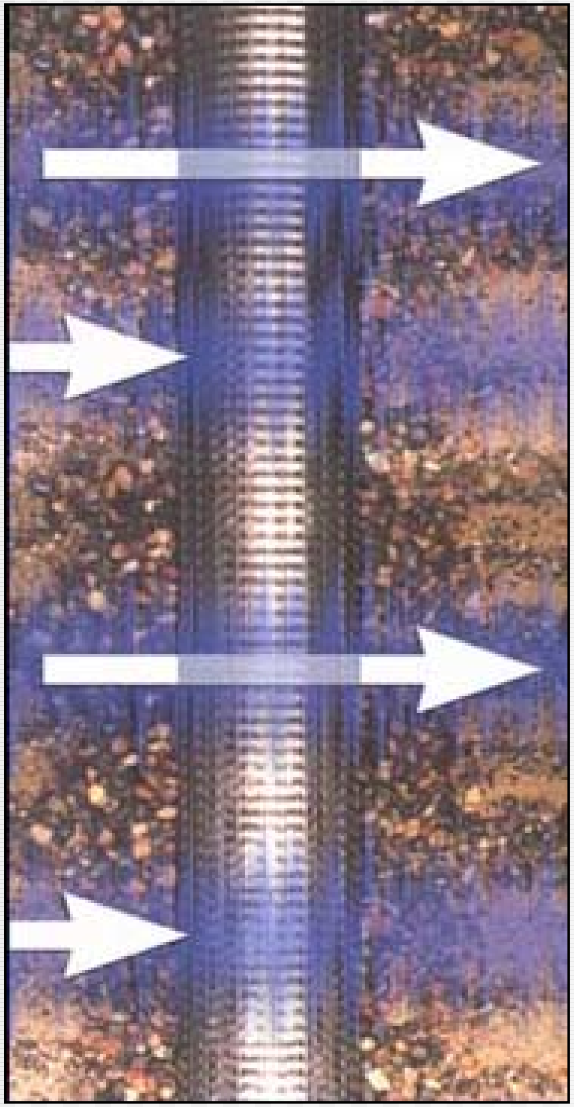
Effects of Ground-Water Velocity (v) on Contaminant Transport



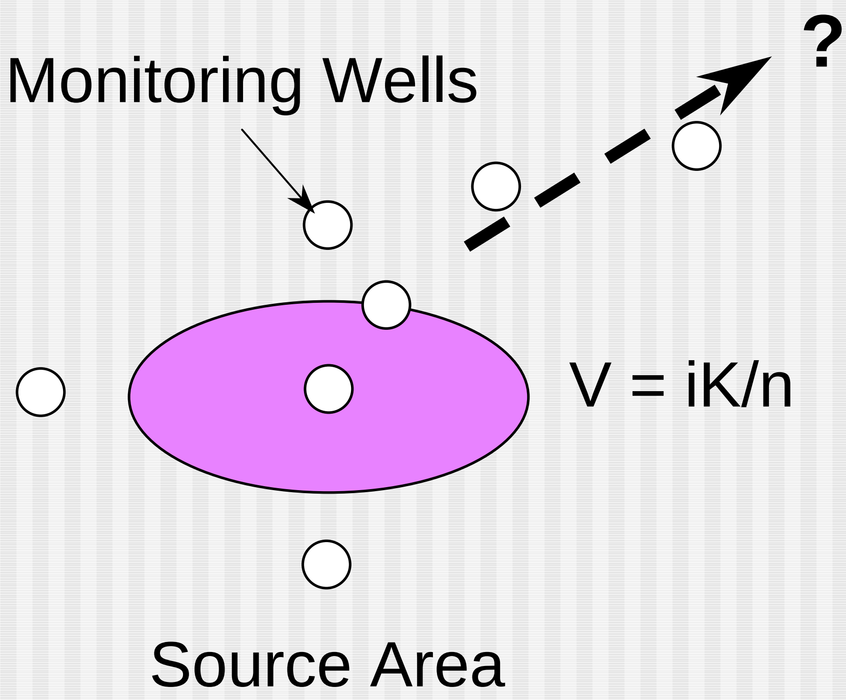
Vertical Zonation of K Should Affect Monitoring Well Design



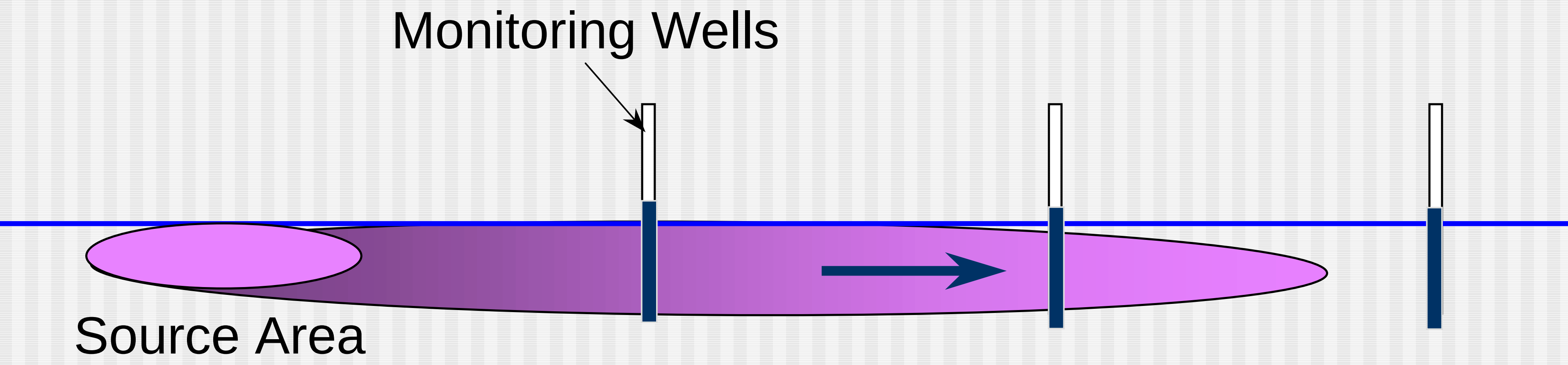
Old Approach, Low Resolution:

- Groundwater flow direction = land topography
- More wells near the source area
- Fewer wells downgradient (nearer the receptors!)
- Wells screened across the water table
- All wells screened at same interval

Problem:
Where is GW (and contaminants) Flowing?

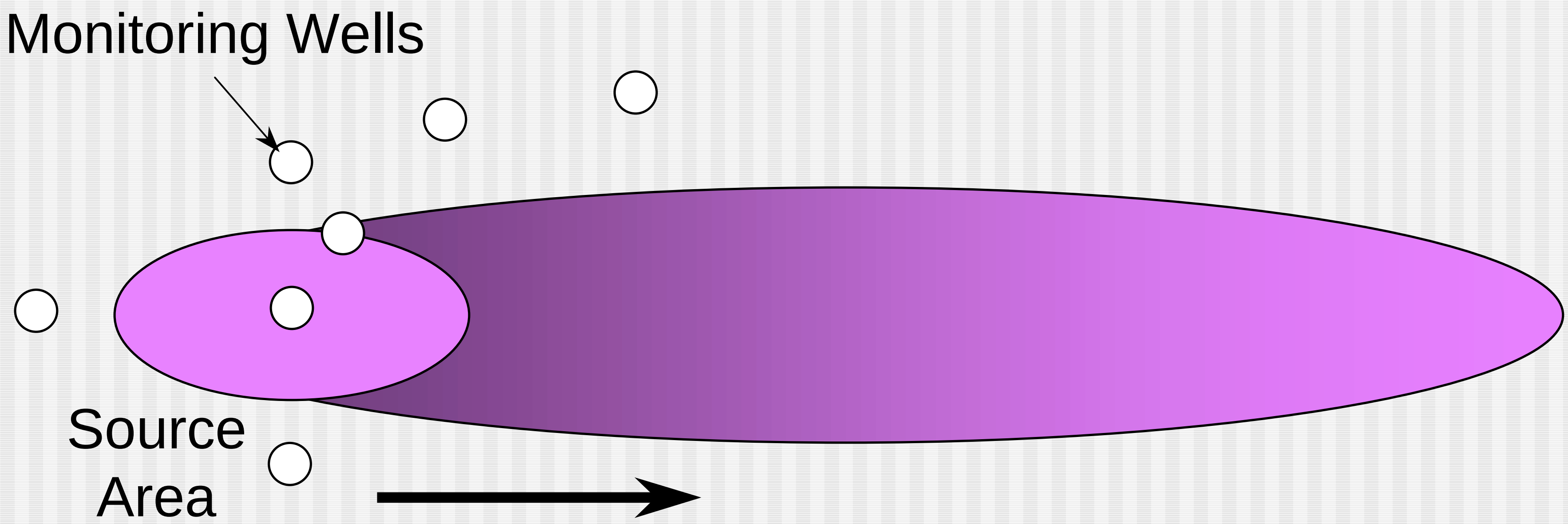


Problem:
Assume Dissolved-Phase will be Near Water Table



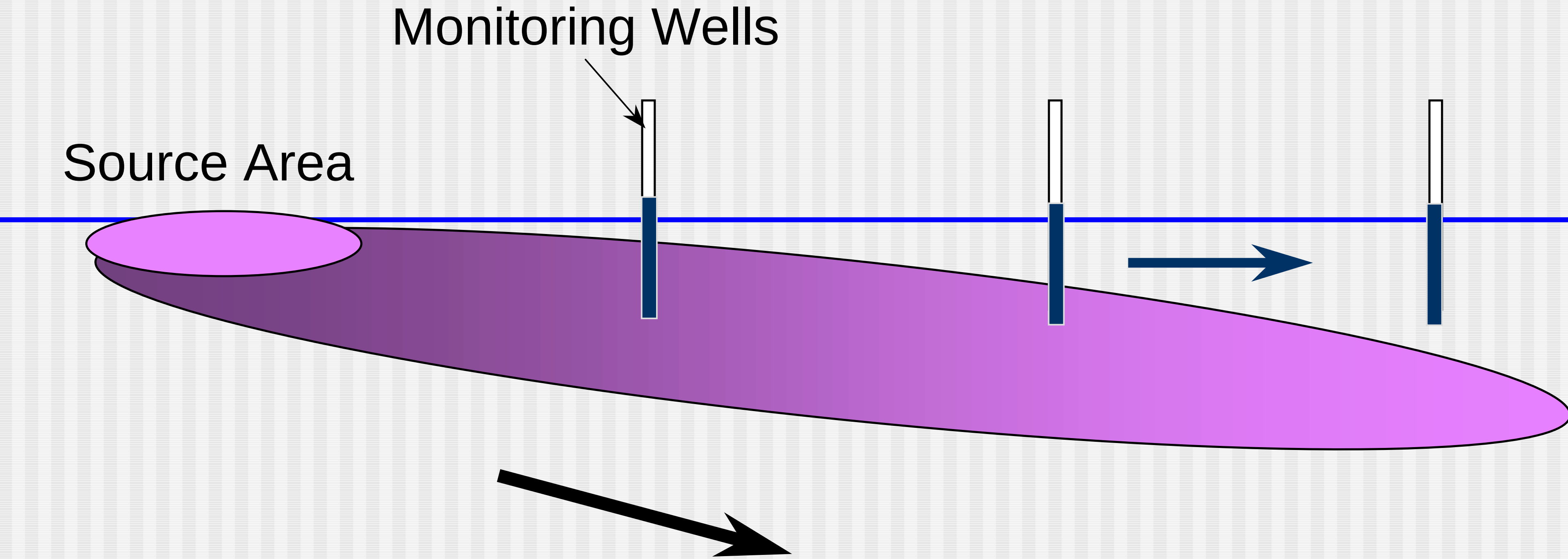
Result?

Monitoring Wells Often Missed the Plume (Plan View)



Result?

Monitoring Wells Often Missed the Plume Vertically



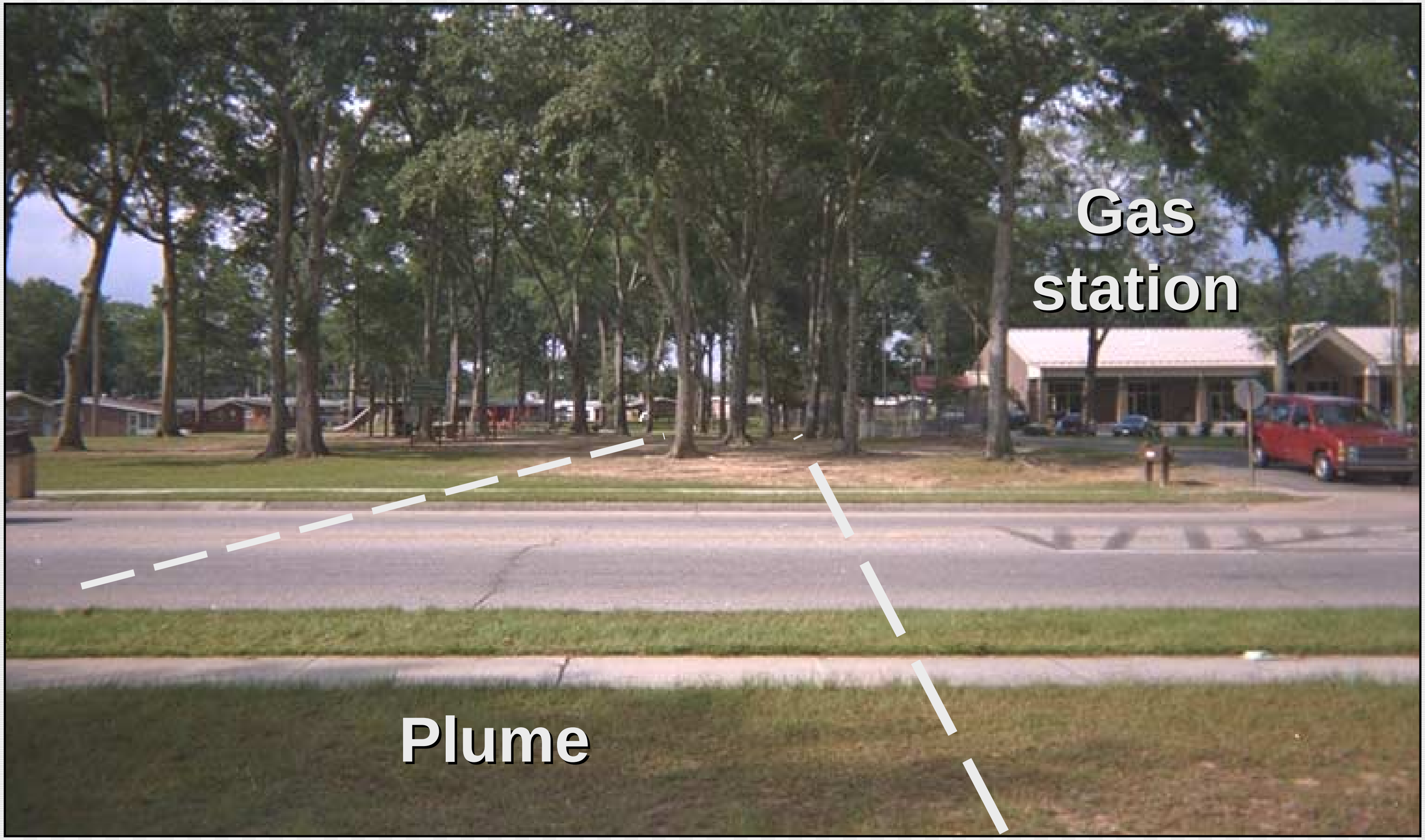
Two Navy Site Examples:

- Tank Farm C, Beaufort, SC

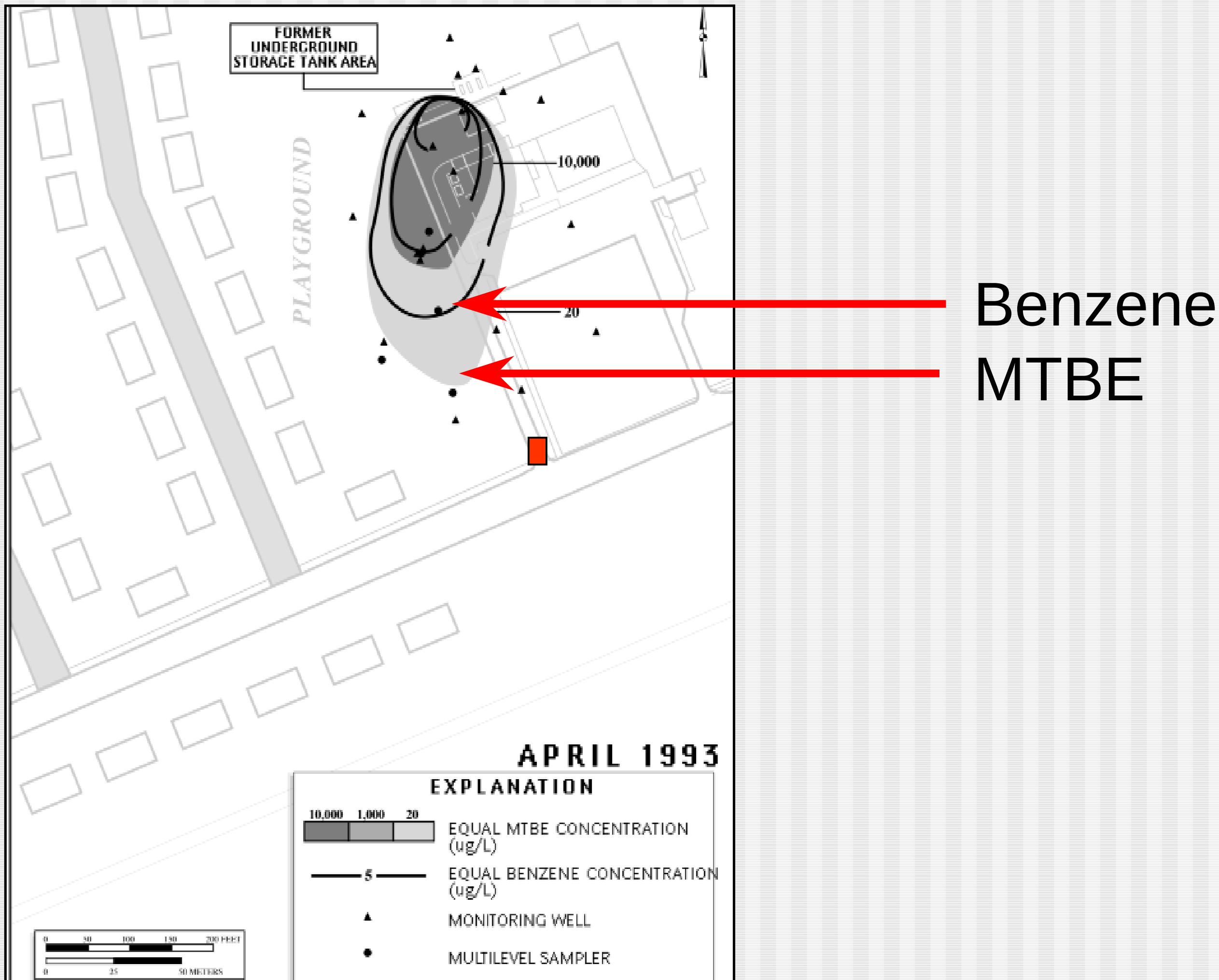
  (Chapelle, Landmeyer, and Bradley, 1996)
- Laurel Bay, Beaufort, SC

  (Landmeyer, Chapelle, Bradley, 1996)

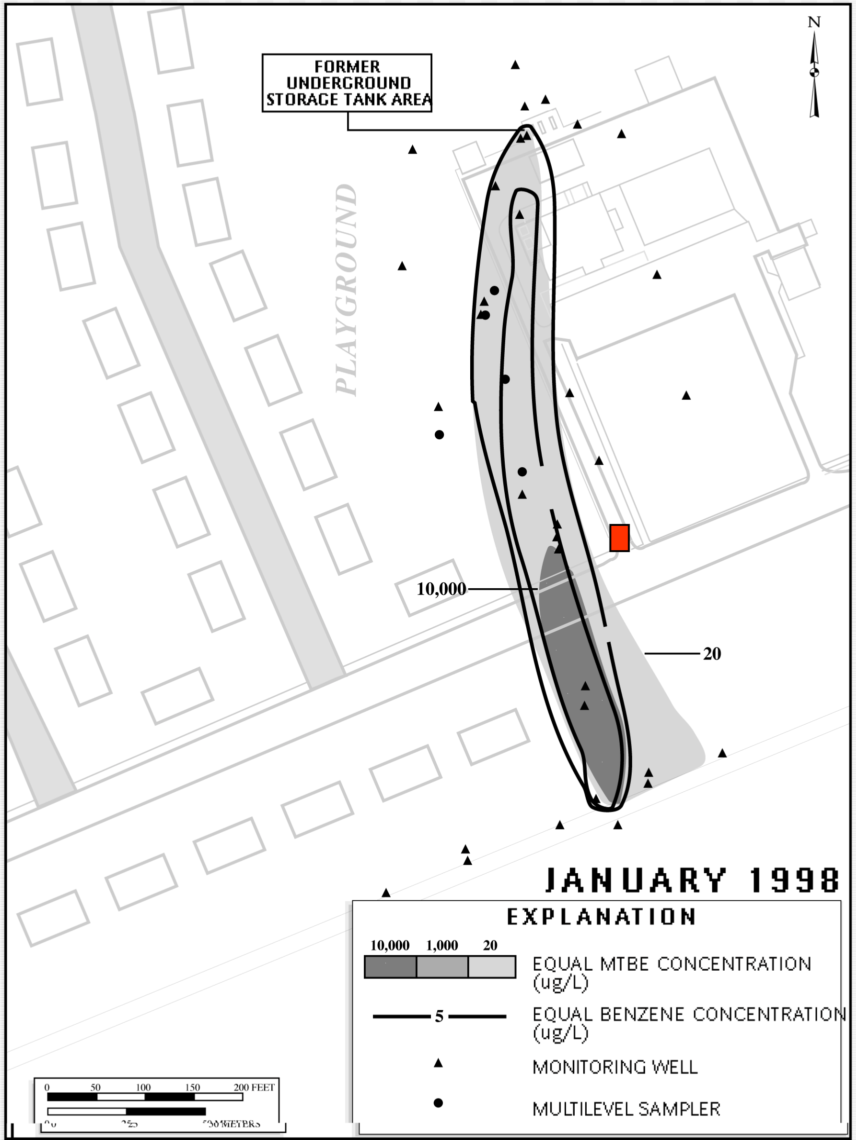
Laurel Bay Gasoline Station, MCAS Beaufort, SC



April 1993
Laurel Bay Gasoline Station, MCAS Beaufort, SC

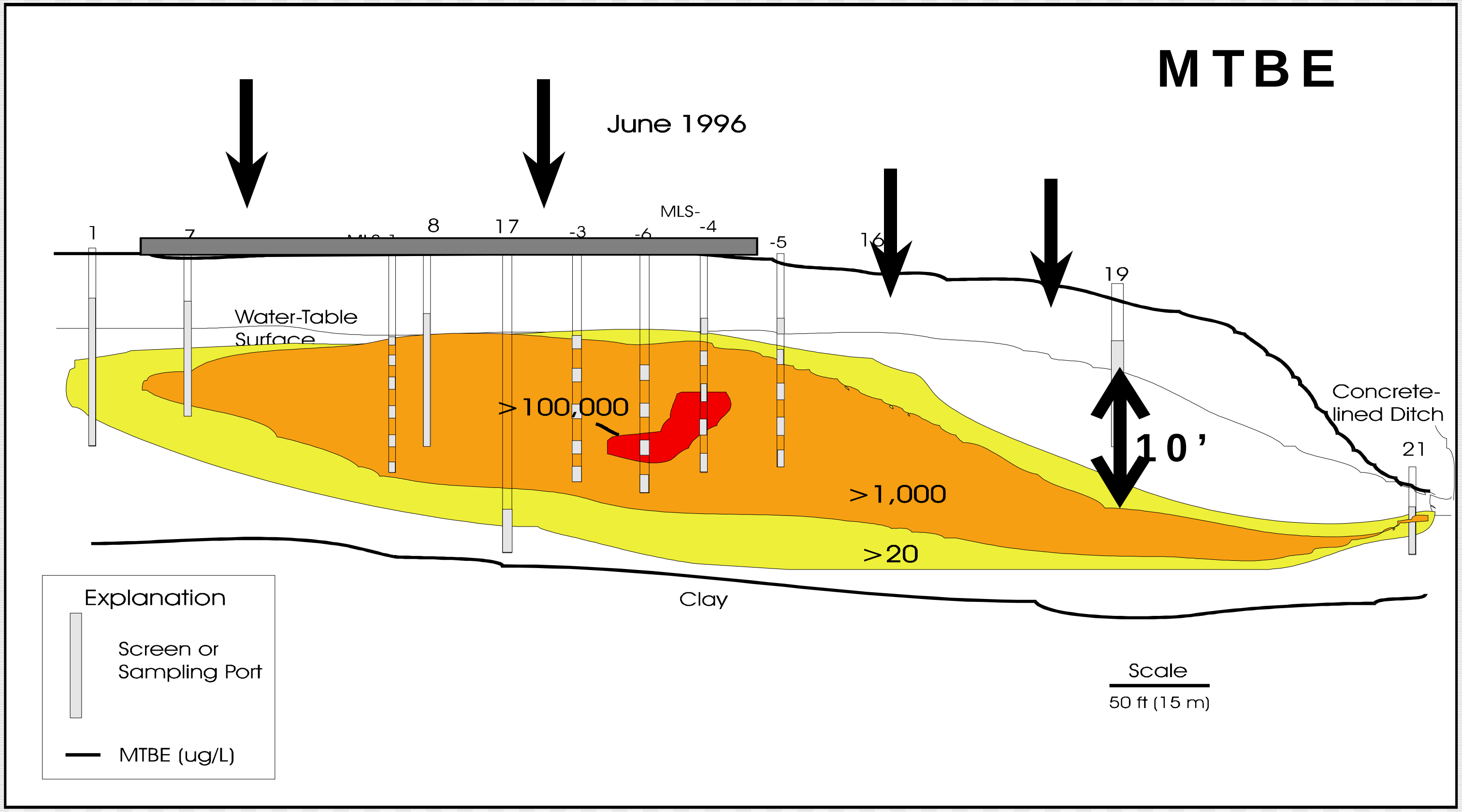


January 1998
Laurel Bay Gasoline Station, MCAS Beaufort, SC



June 1996
Laurel Bay Gasoline Station, MCAS Beaufort, SC

No Recharge
Recharge



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  - Hydrogeology ("Driving Forces")
    - Principles
    - Tools
      - SCAPS
      - Nested Wells
      - Direct Push
  - Geochemistry/Microbiology ("Resisting Forces")
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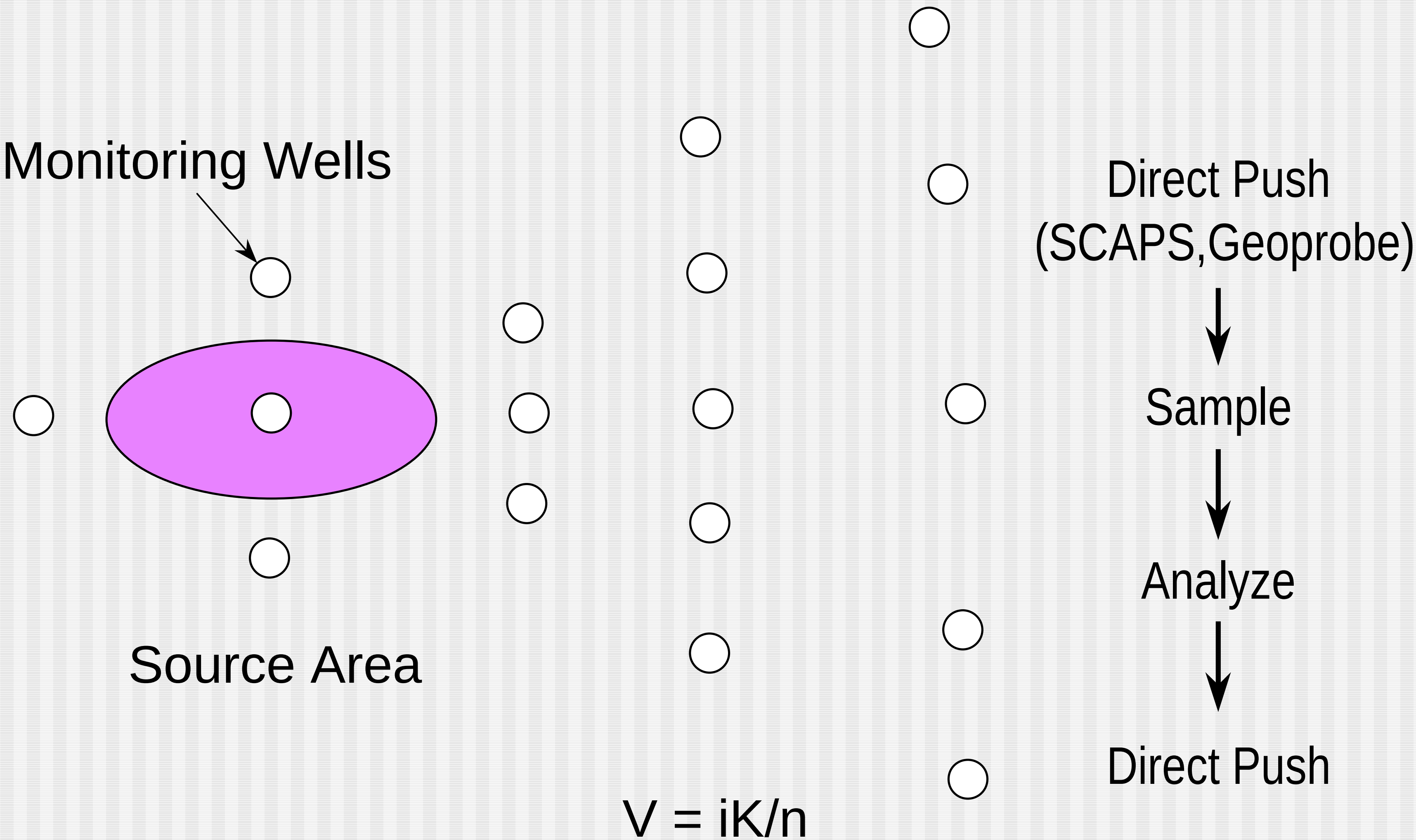
Solution: Higher Resolution Hydrogeologic Site Characterization Tools

- Direct-push (Geoprobe)
- SCAPS Rig
- Waterloo sampler
- Hydropunch samples
- Cone penetrometer
- Borehole flowmeters
- Nested monitoring wells

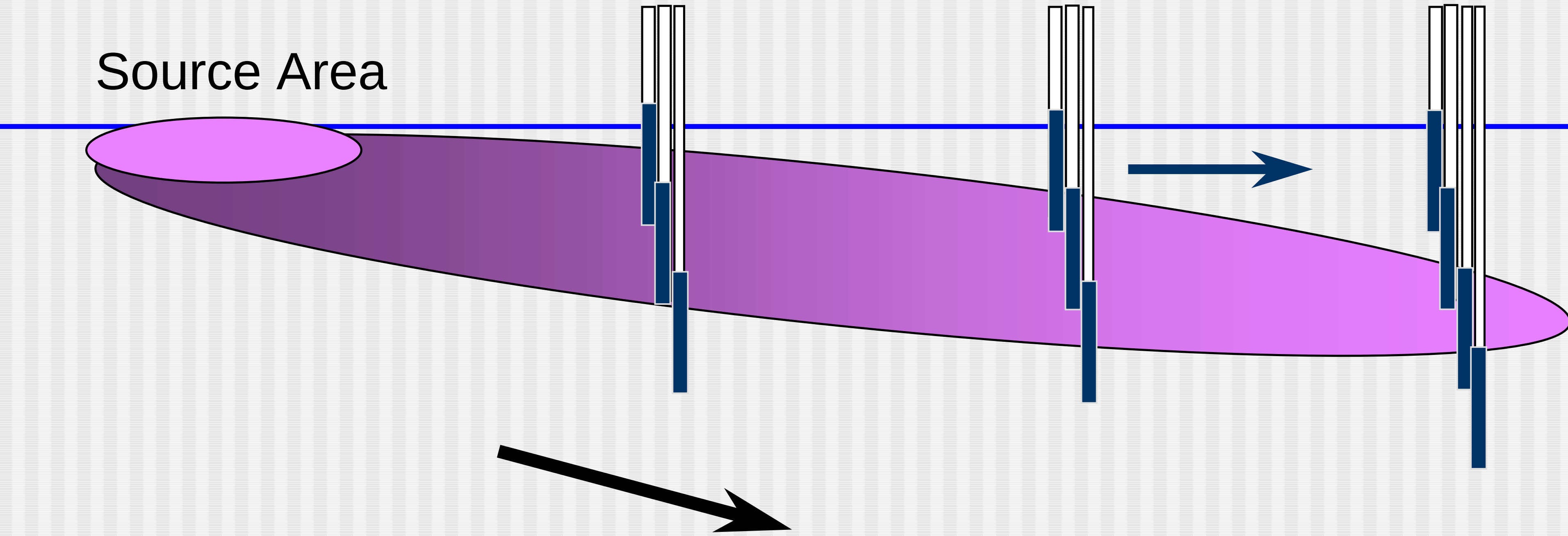
Goal = Near real-time sampling-interpretation feedback

Solution: Use Near "Real-Time" Field Techniques

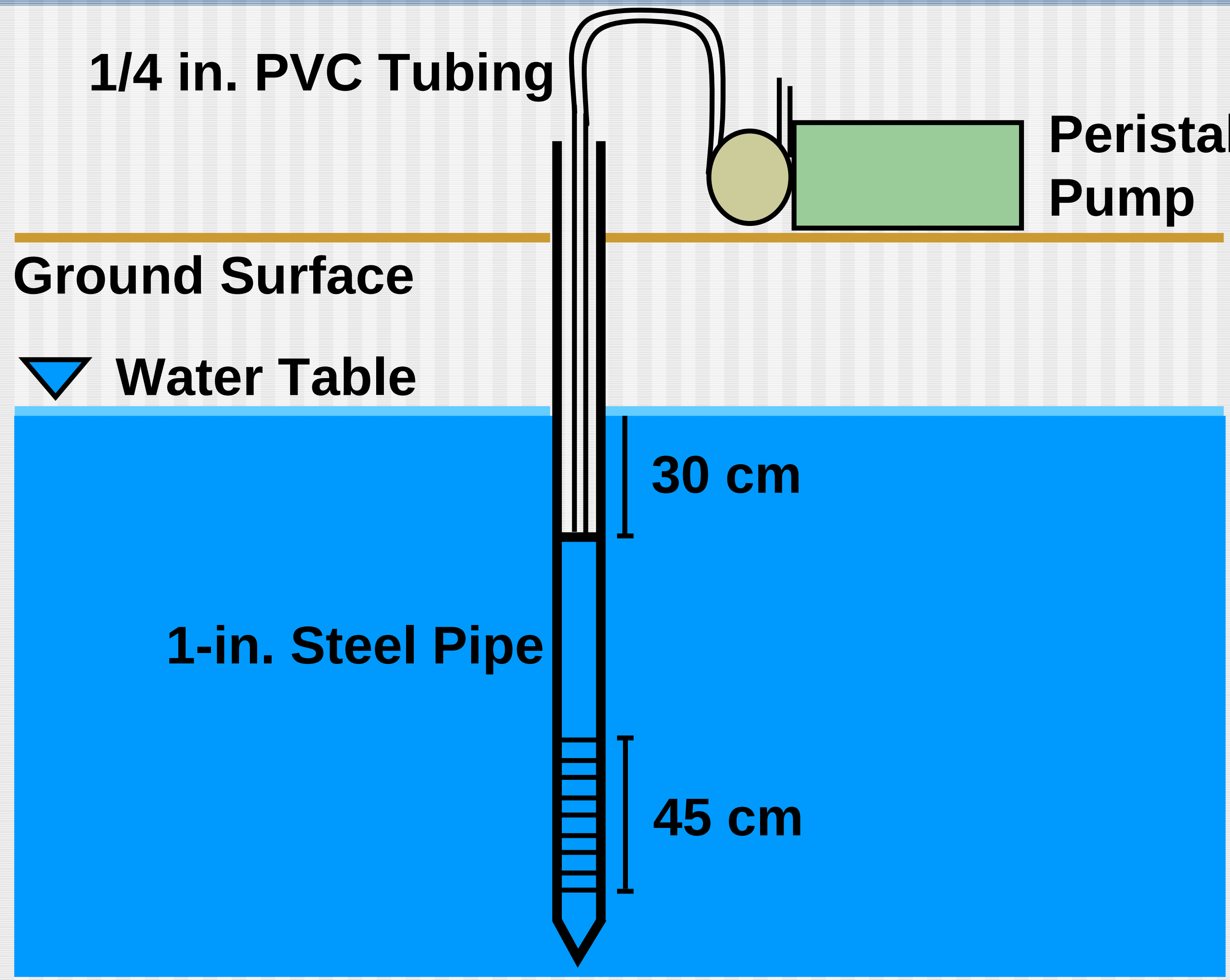


Solution: Use Nested Wells

"The farther your groundwater flows, the deeper your wells should go"



Direct-Push Approaches: Geoprobe falling-head slug tests - k



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    - Principles
      - Redox
      - Dissolved Hydrogen (DH) Monitoring
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Why is Assessing Geochemistry Important to MNA?

- Groundwater geochemistry is a record of ongoing chemical, physical, and microbial processes
- The efficiency of monitored natural attenuation can often be determined from groundwater chemistry information (i.e., redox conditions)

What is a Redox Process?

- Electrons that are transferred in chemical or biochemical reaction

$$CH_{2n}O + O_2 \longrightarrow CO_2 + e^-$$

$$CH_{2n}O + O_2 \longleftarrow H_2O + CO_2$$

In a Redox Reaction

One compound <u>donates</u> an electron and another compound <u>accepts</u> an electron:

- Benzene + $O_2 \longrightarrow CO_2 + e^-$
  (Benzene is electron donor)

- e^- + TCE $\longrightarrow$ DCE + Cl^-
  (TCE is electron acceptor)

Electron Flow

- The flow of electrons from donors to acceptors is capable of doing work
- Microorganisms (and everybody else) uses the work done by flowing electrons to support life functions

e-donor (organic carbon)

e-acceptor
O_2, NO_3, Fe^{3+},
SO_4^{2-}, CO_2, (TCE)

Biodegradation of PHs is Electron-Donating Process

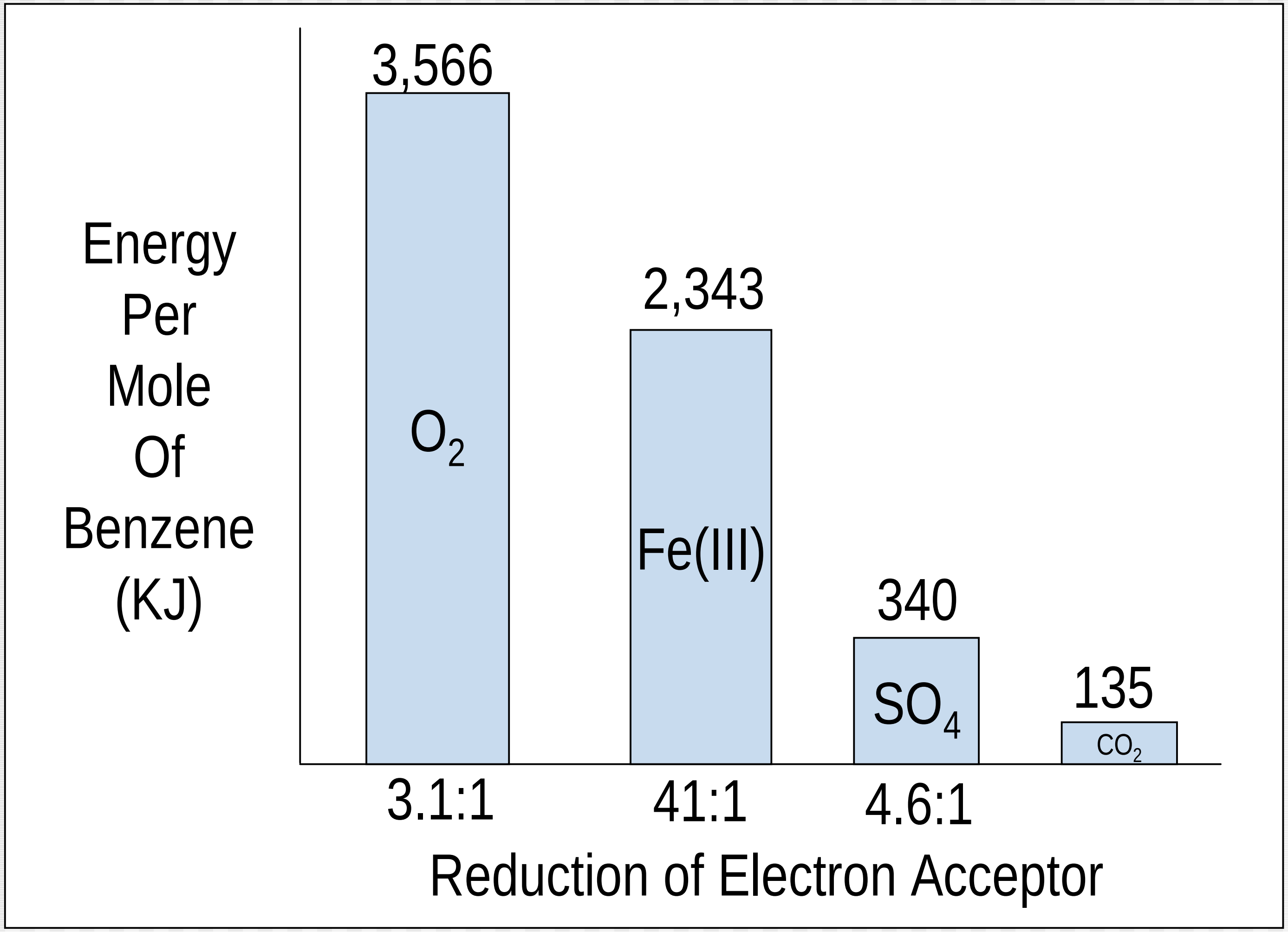
- Benzene $\longrightarrow$ $CO_2 + e^-$ (benzene donates e^-)

- $2e^- + \underbrace{O_2}_{\text{Electron Acceptor}} \longrightarrow 2H_2O$ (oxygen accepts e^-)

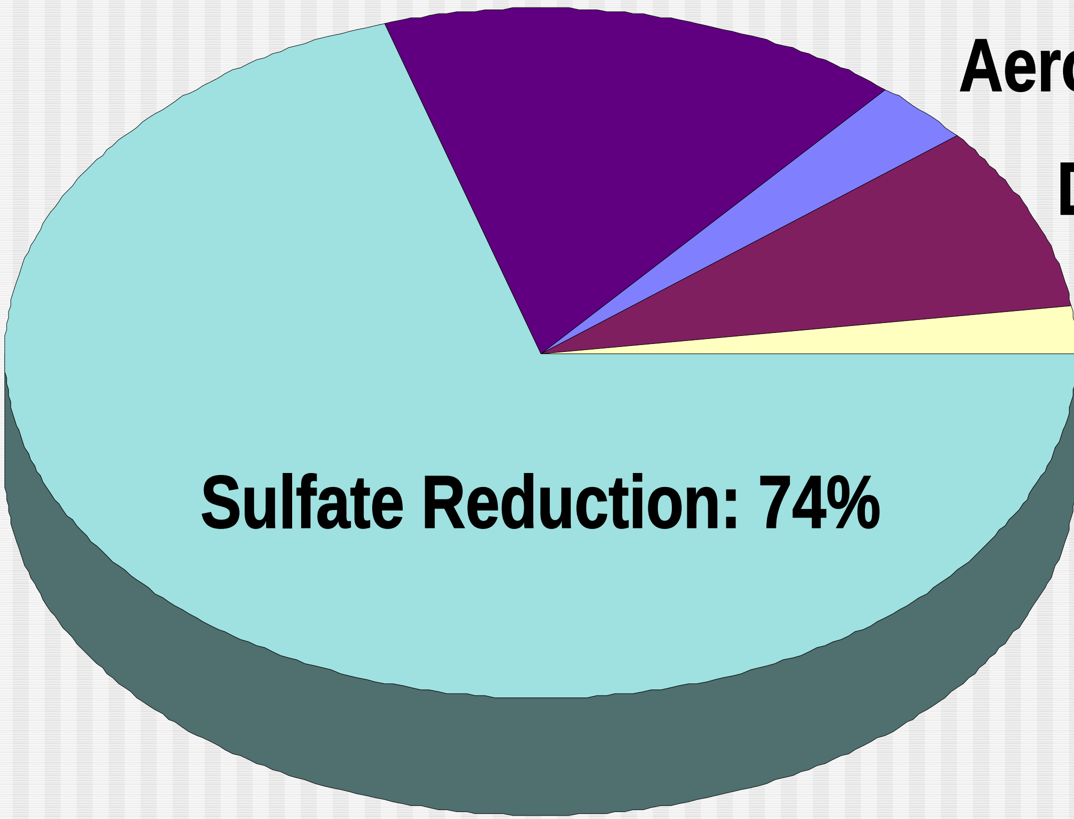
Because the Biodegradation of PHs is Electron-Donating Process:

- The availability of electron acceptors determines the rate and extent of biodegradation
  - Oxygen
  - NO_3
  - Fe(III)
  - Mn(IV)
  - Sulfate
  - CO_2
  - Chlorinated solvents!

Electron-Accepting Process Sequence



Relative Importance of Biodegradation Mechanisms

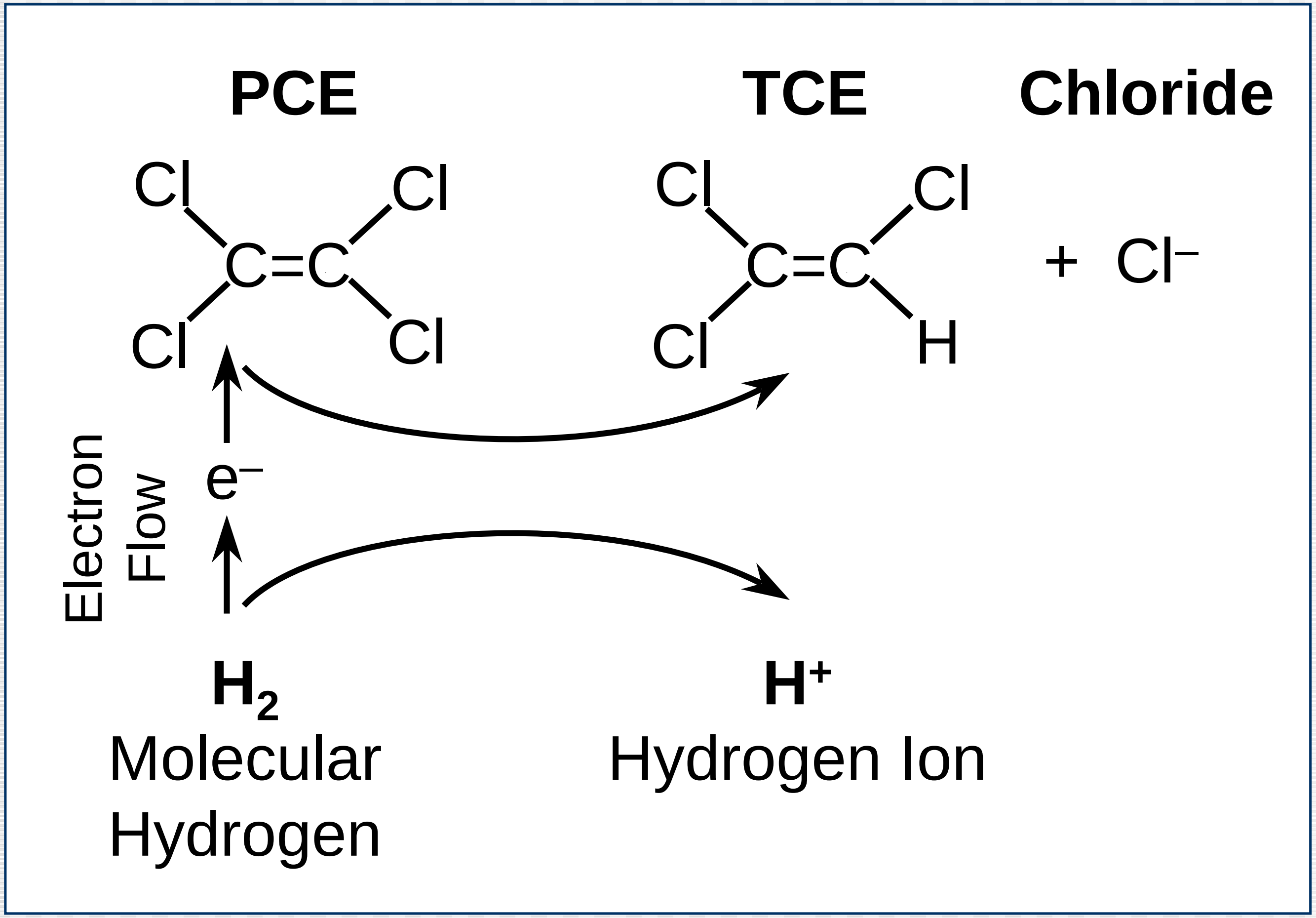


Based on 42 sites

Monitoring for Geochemical Indicators of MNA

Analytical Parameter	Field or Laboratory Parameter	Method of Analysis
Dissolved oxygen (DO)	Field	Meter, field kit titration
Nitrate (NO_3)	Laboratory	Ion Chromatography
Nitrite (NO_2)	Laboratory	Ion Chromatography
Dissolved ferrous iron (Fe^{2+})	Field	Field kit spectrophotometer
Sulfate (SO_4)	Laboratory	Ion Chromatography
Hydrogen sulfide (H_2S)	Field	Field kit spectrophotometer
Dissolved Methane (CH_4)	Laboratory	GC FID
pH (units)	Field	Meter
Eh (redox potential)	Field	Meter
Dissolved Hydrogen (H_2)	Field	Gas chromatography

Molecular Hydrogen (H_2) Drives Reductive Dechlorination

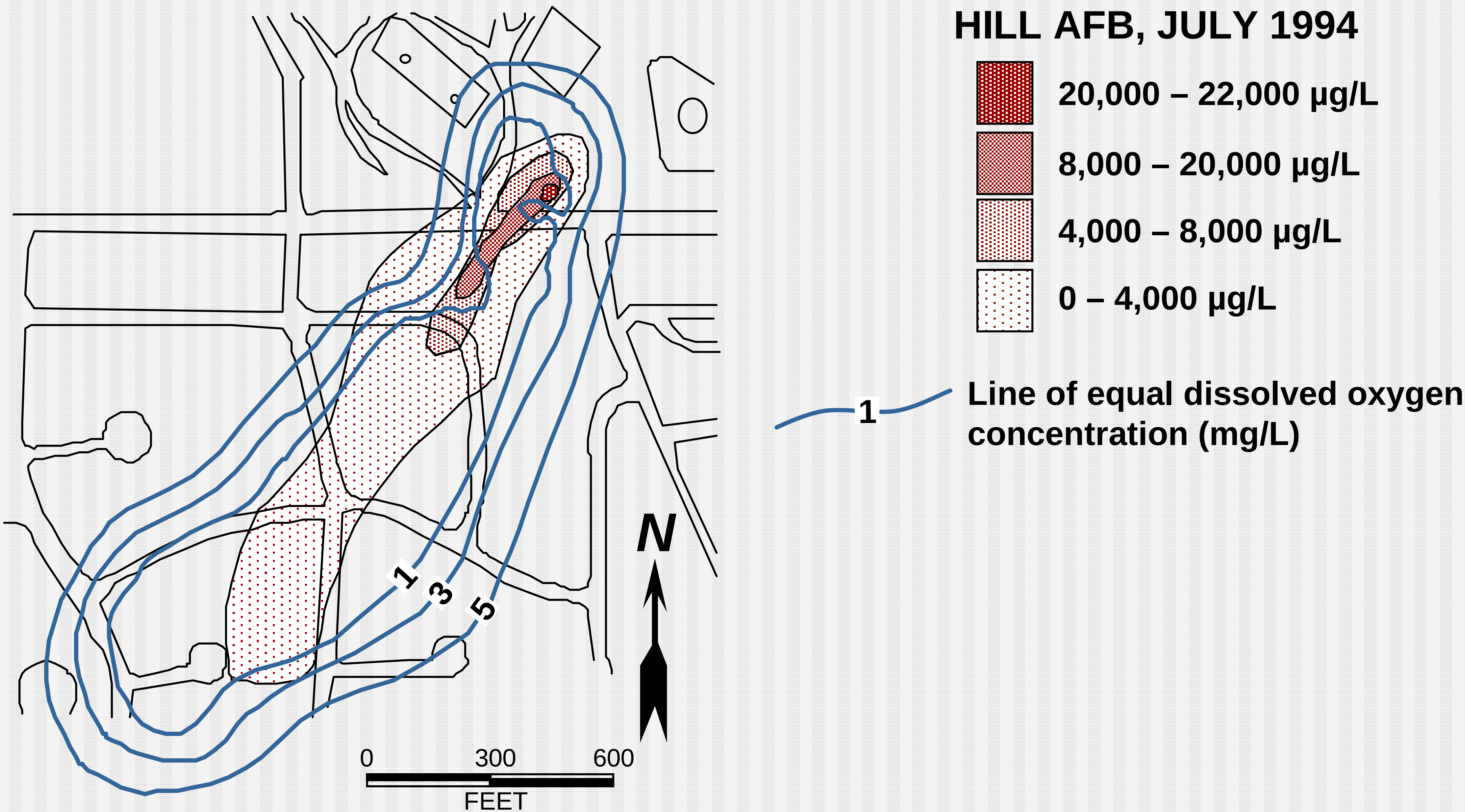


Source: Gosset and Zinder, 1996

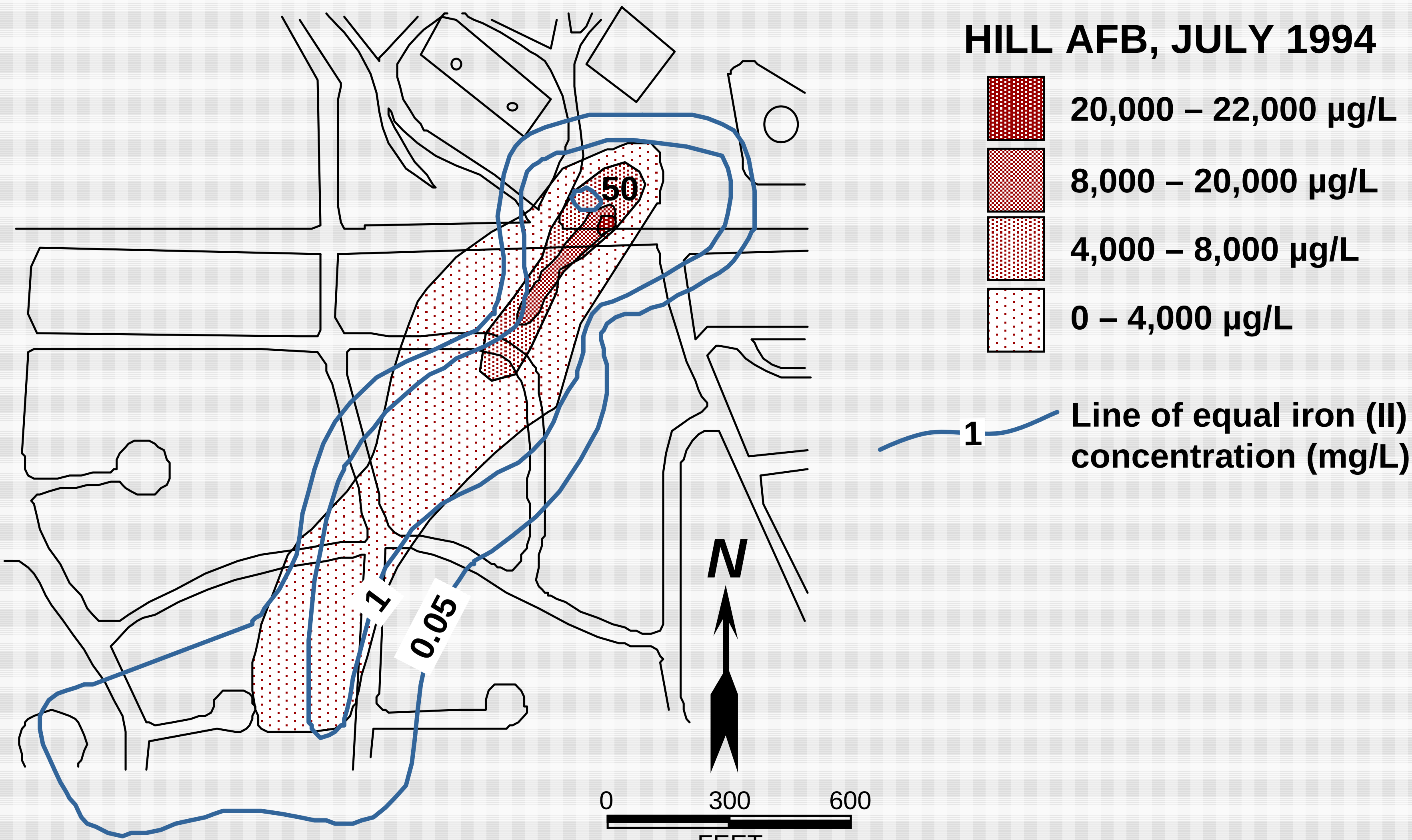
What about Redox Processes over space?

Hill AFB Example

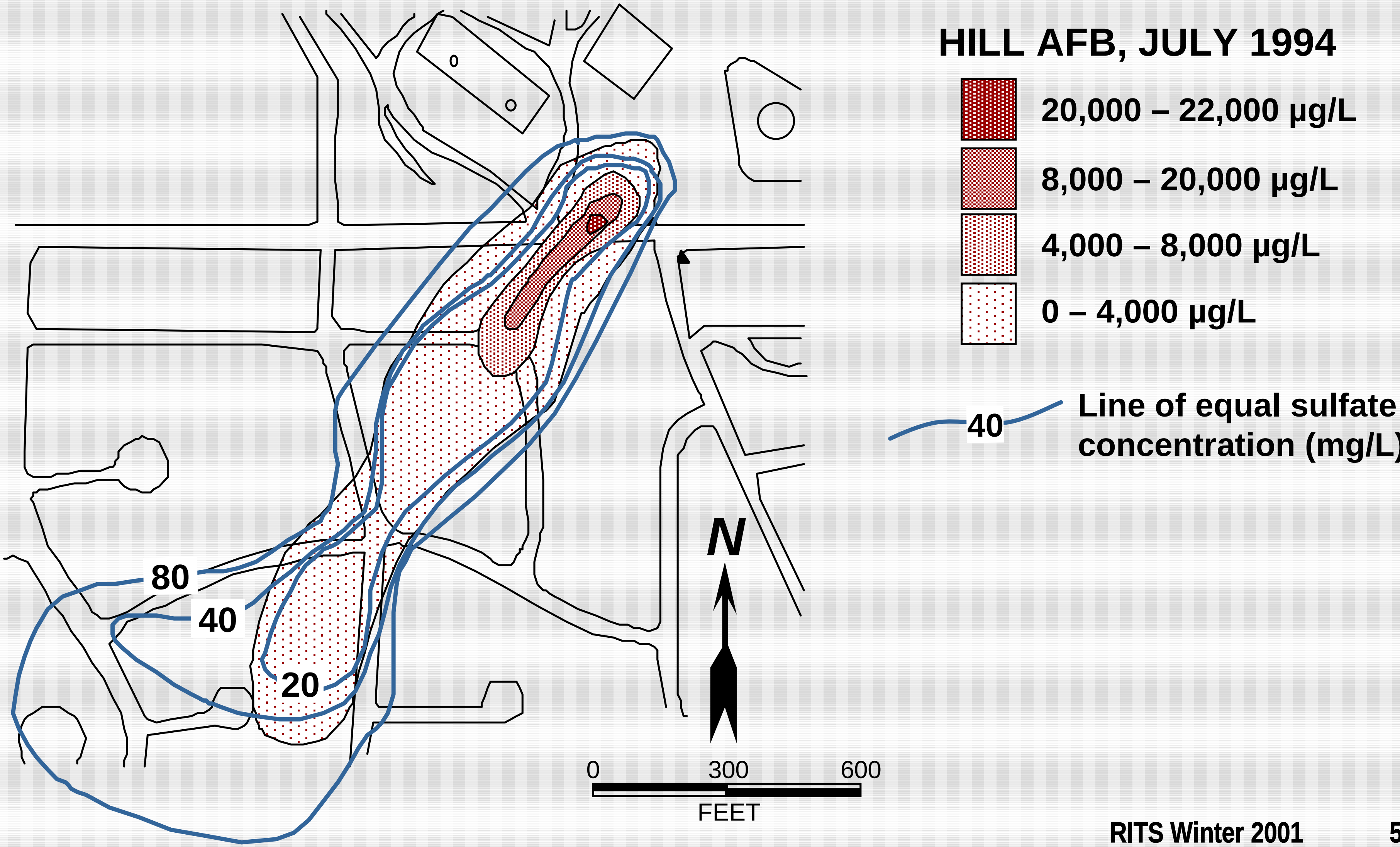
Total BTEX and Dissolved Oxygen



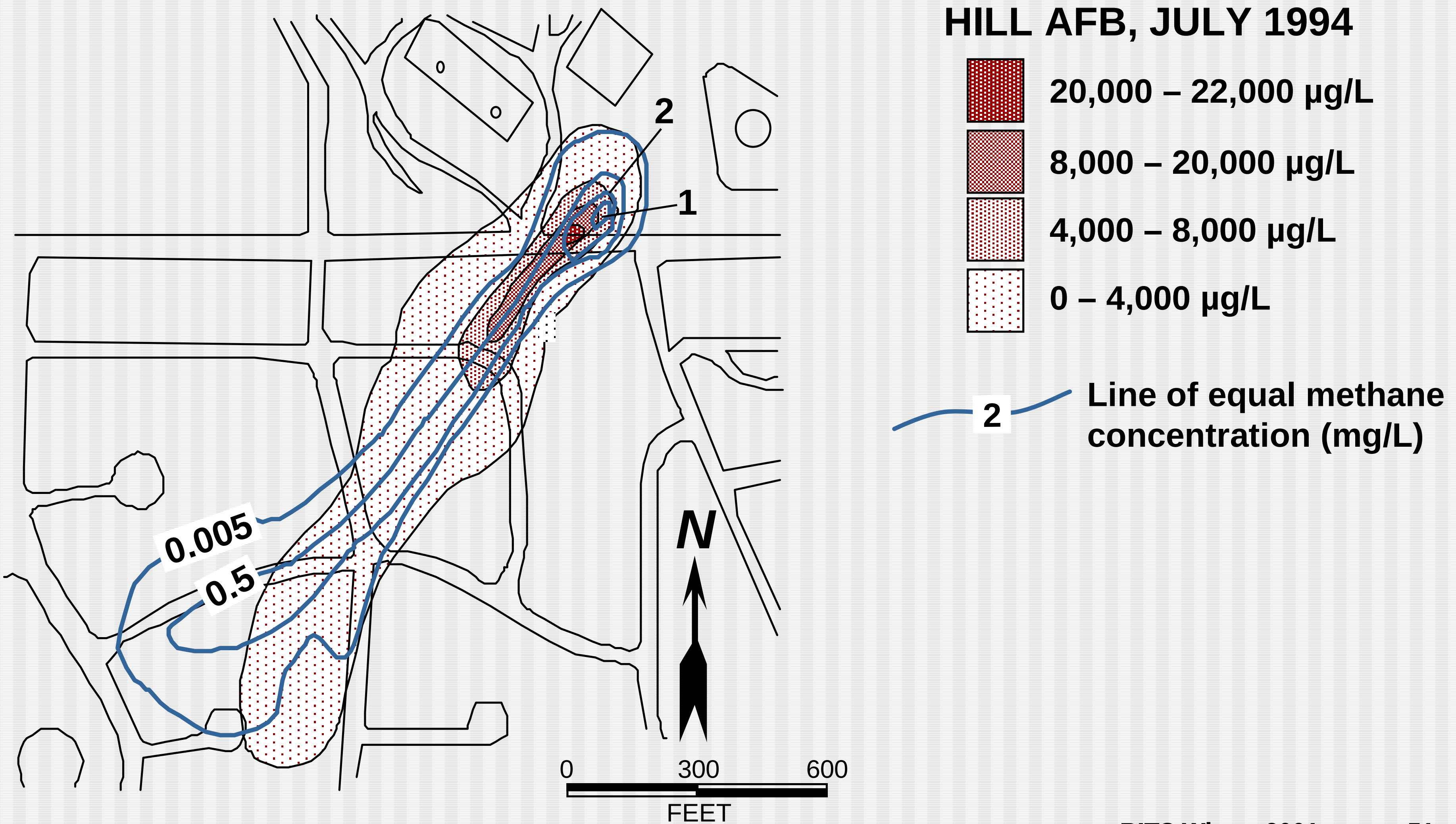
Total BTEX and Iron (II)



Total BTEX and Sulfate



Total BTEX and Methane

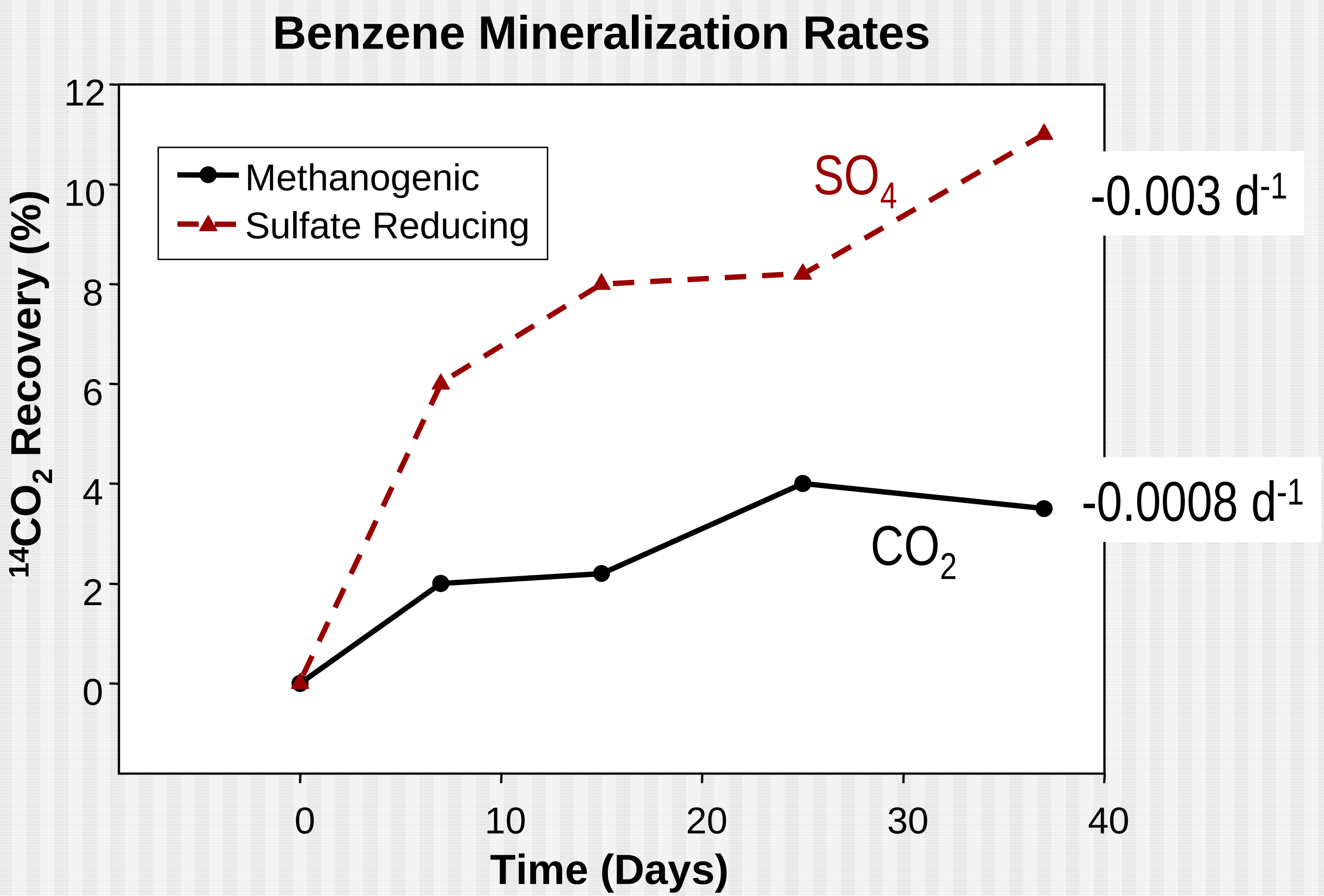


What about Redox Processes over time?

Laurel Bay Example

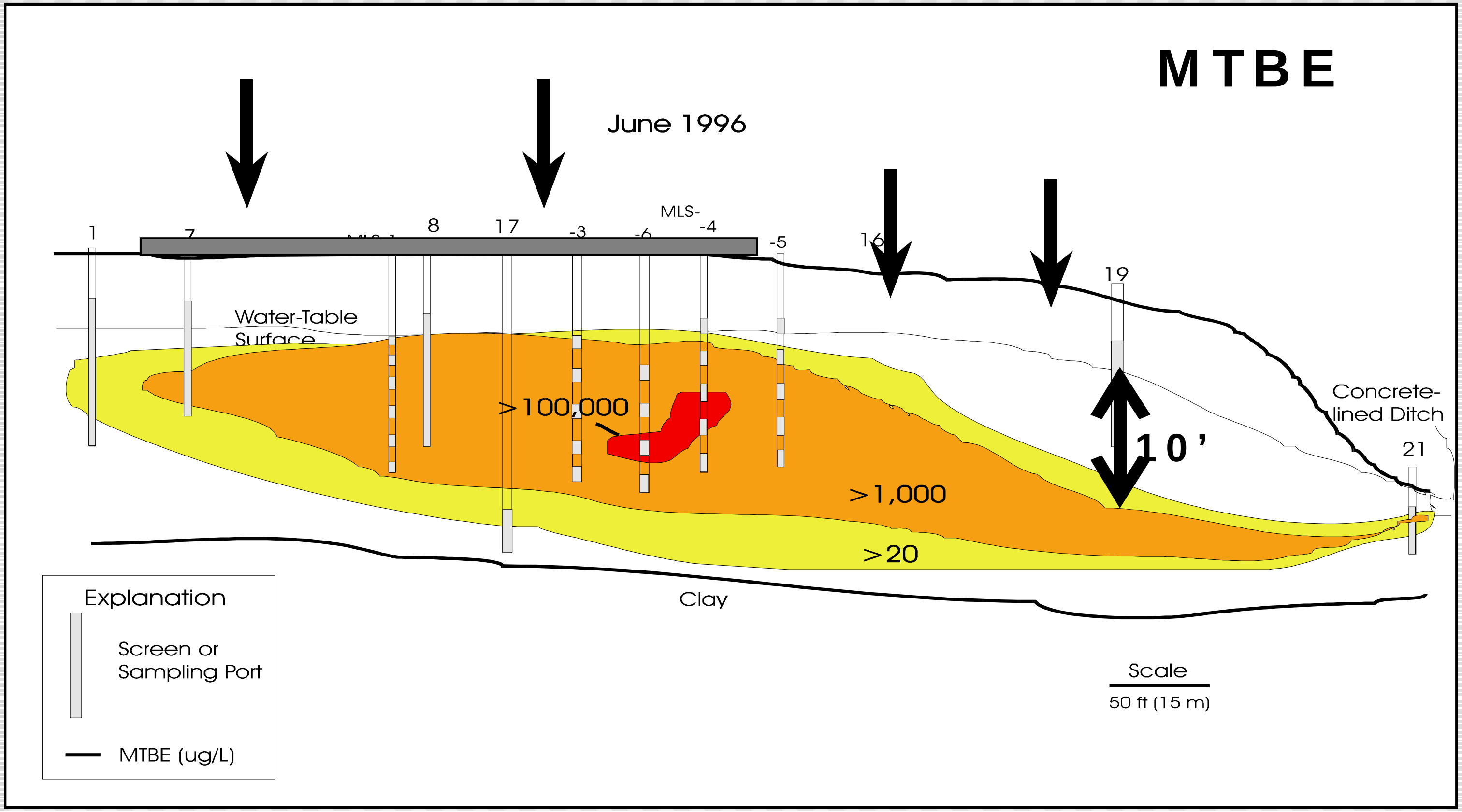
Francis H. Chapelle
Paul M. Bradley
and
James E. Landmeyer

Biodegradation Rates Depend on Ambient Redox Conditions

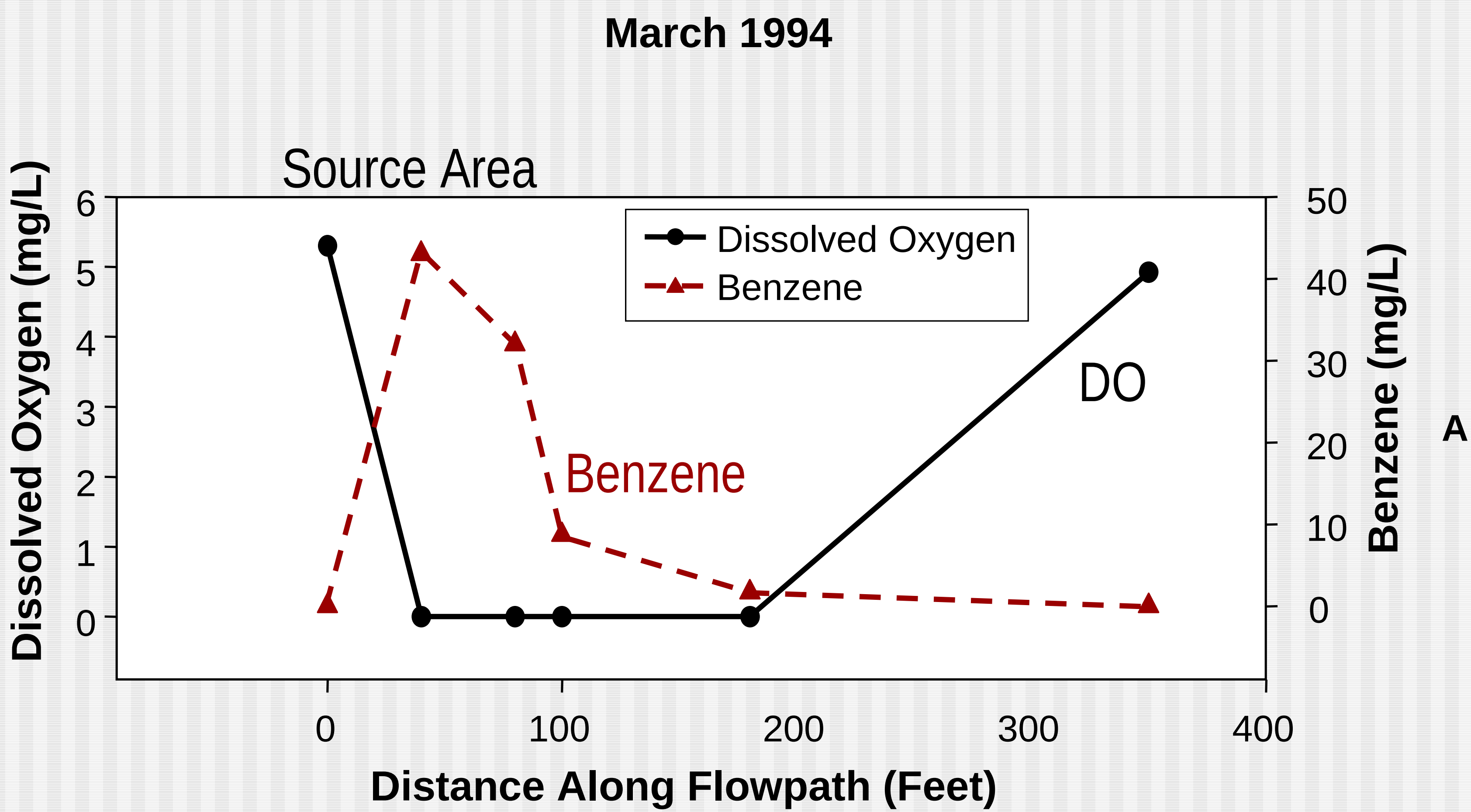


June 1996
Laurel Bay Gasoline Station, MCAS Beaufort, SC

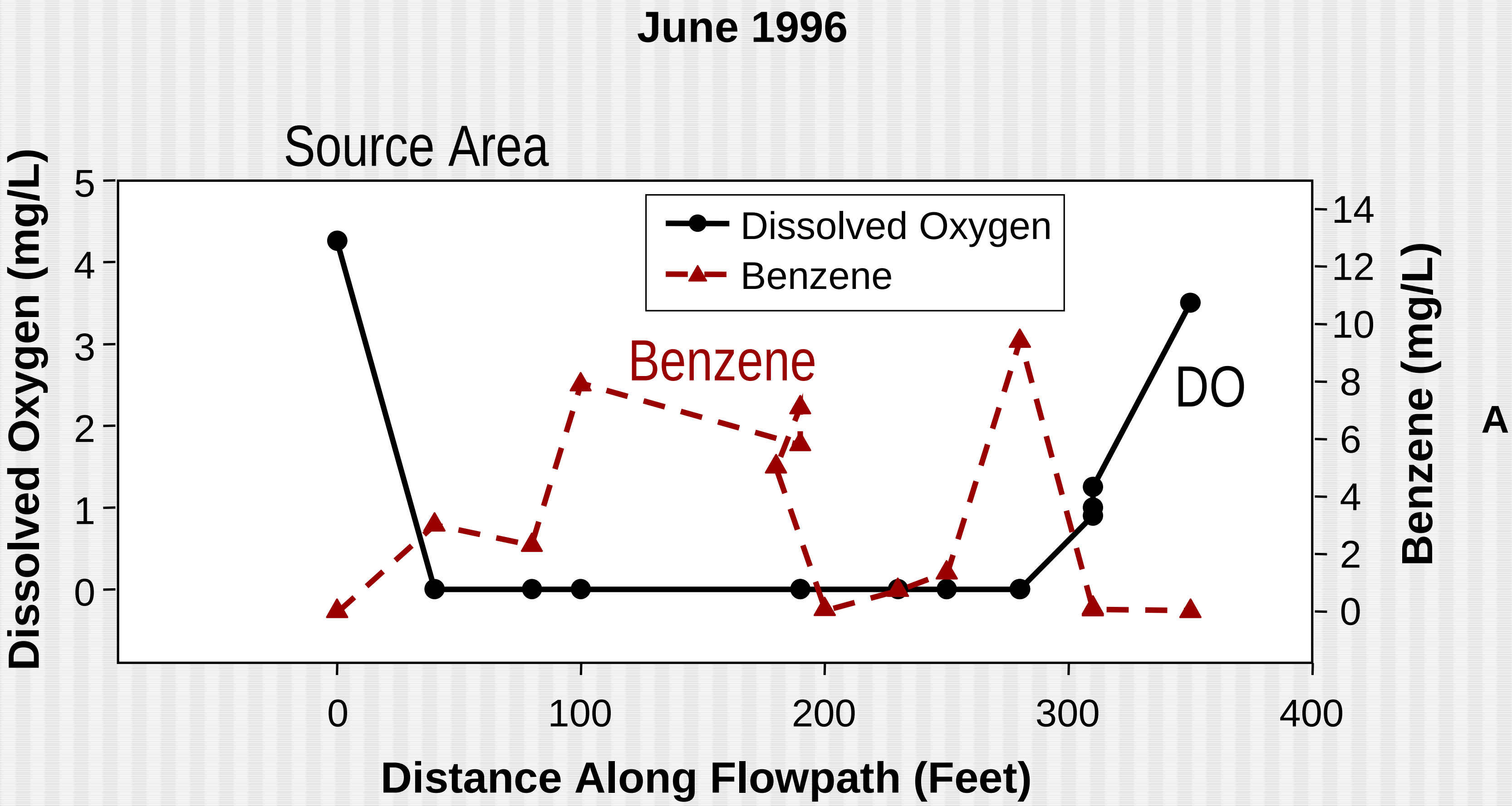
No Recharge Recharge



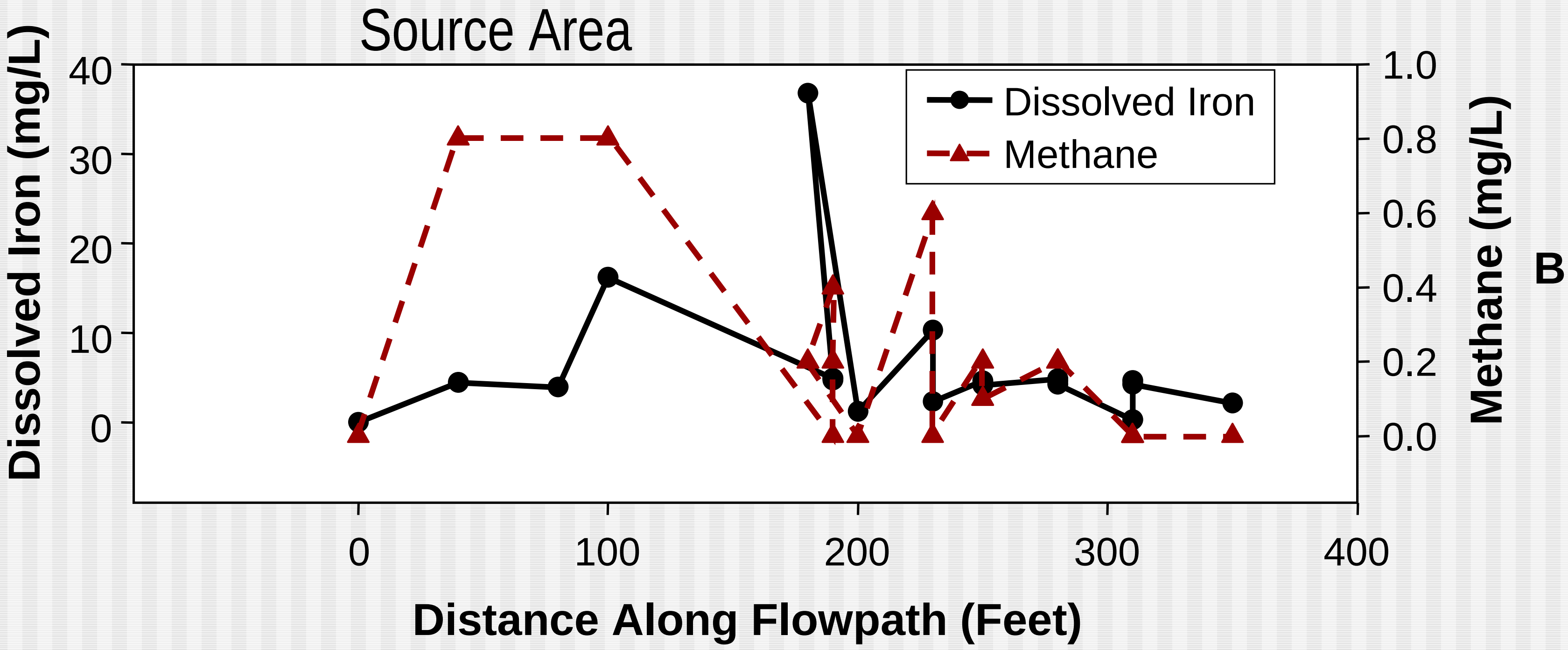
Early (1994) Depletion of Oxygen



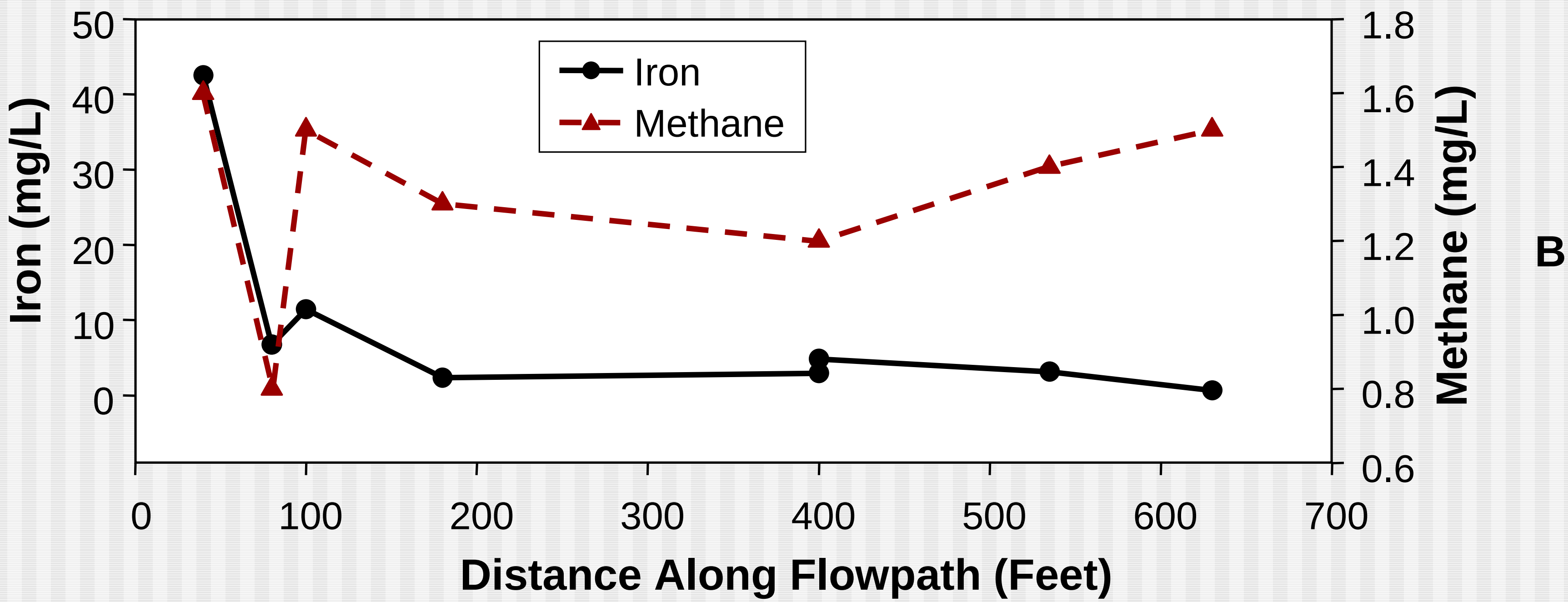
By 1996, the Anoxic Zone had Expanded Downgradient



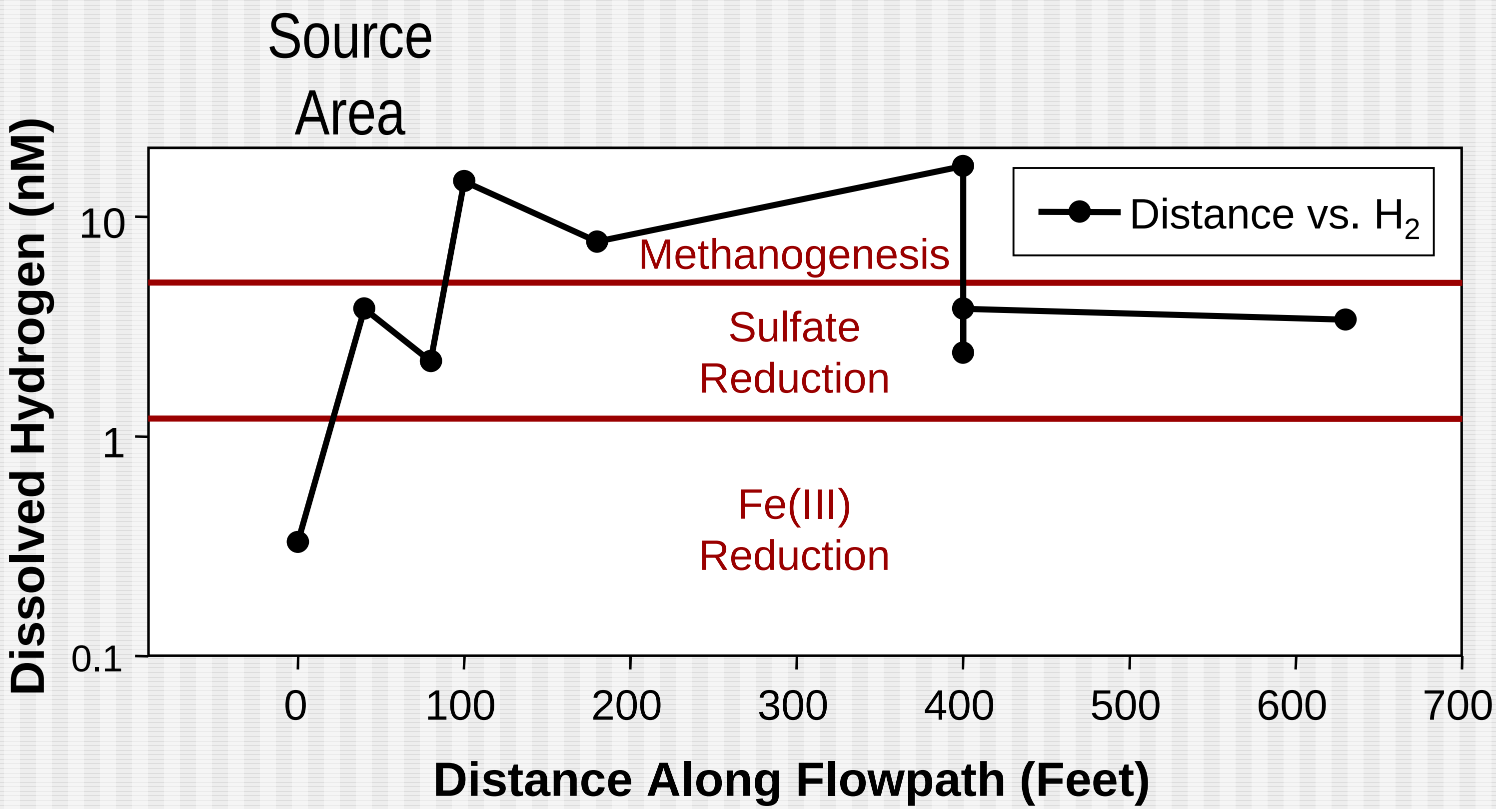
By 1996, Methane Production Had Been Initiated



By 1998, Methane was Present Throughout the Plume



H_2 Concentrations, 2000



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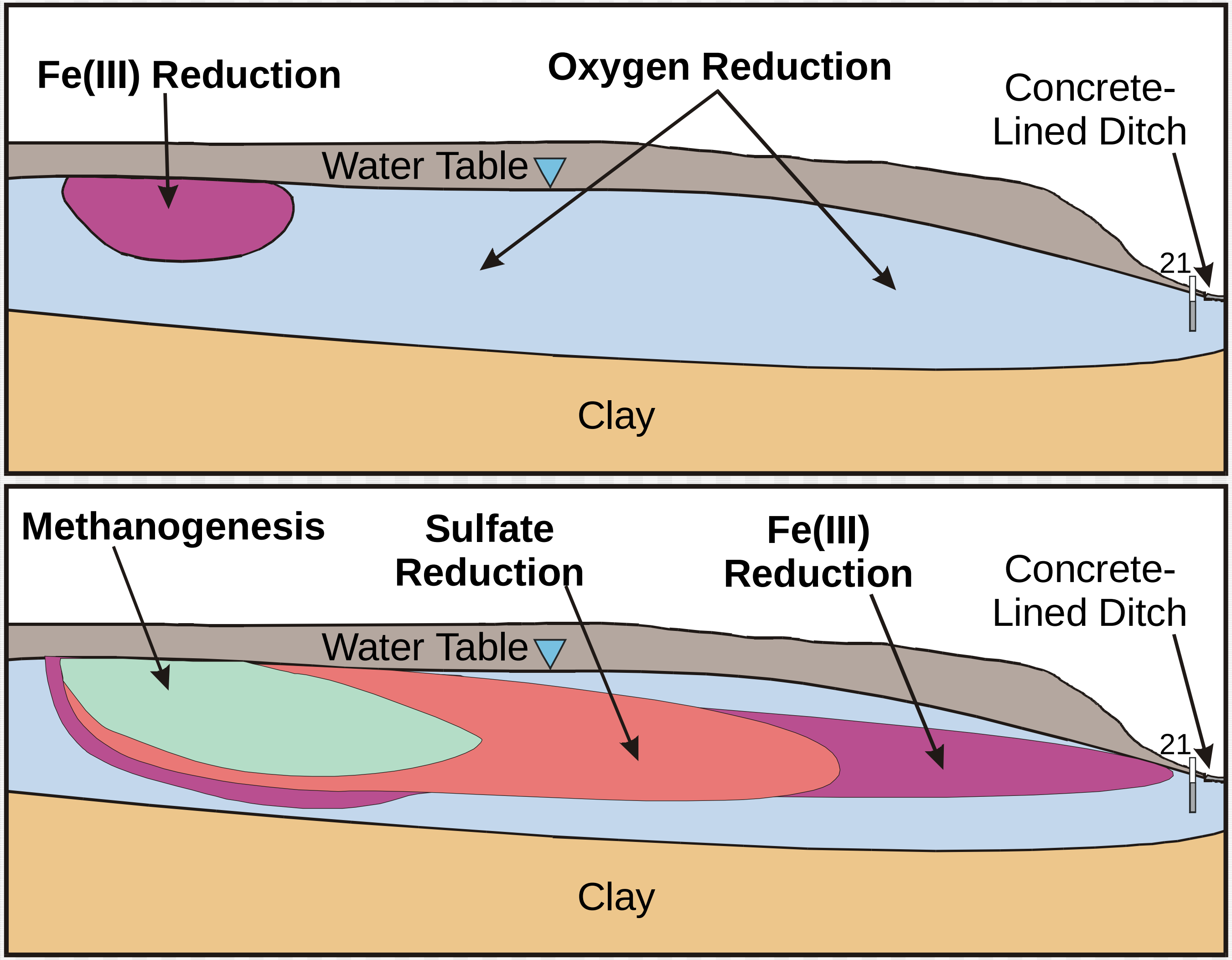
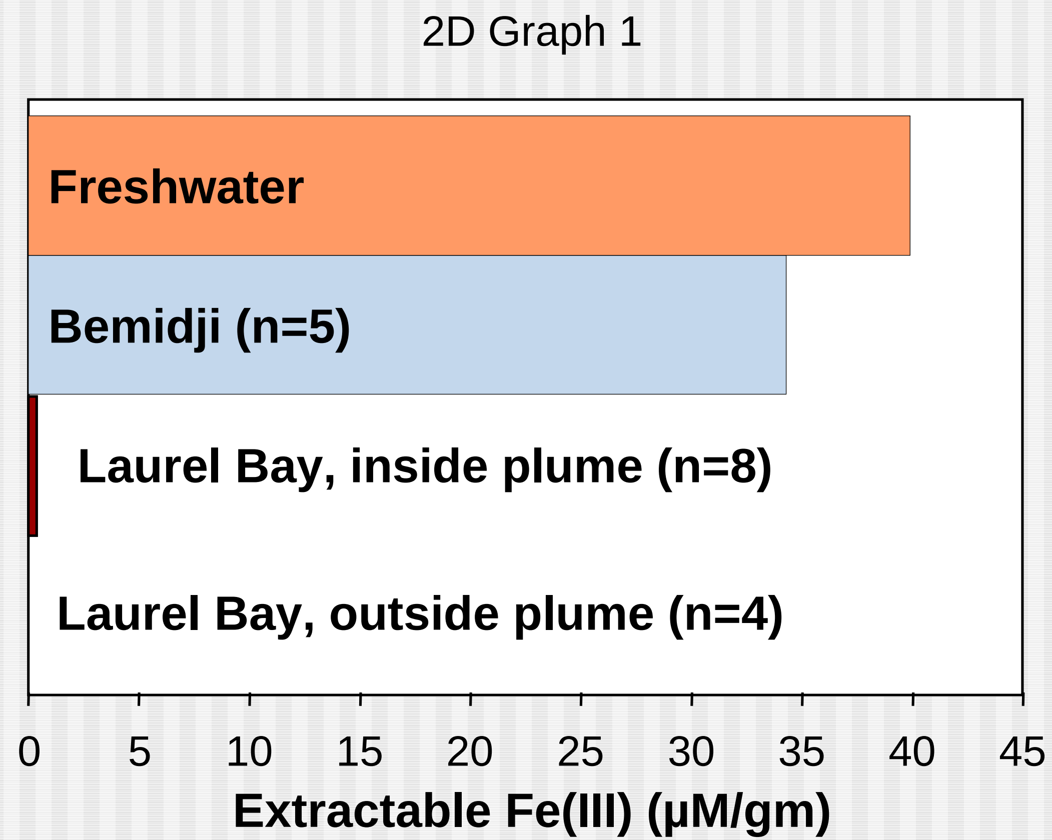
Why Have Redox Conditions Changed so Rapidly?



1994

1998

Extractable Fe(III)



Bemidji Data (Tuccillo, Cozzarelli, and Herman, 1999)

Conclusions

- Redox Conditions Have Changed Rapidly at the Laurel Bay Site
- The Rapid Nature of the Redox Changes Reflects the Relative Lack of Fe(III) in Laurel Bay Sediments

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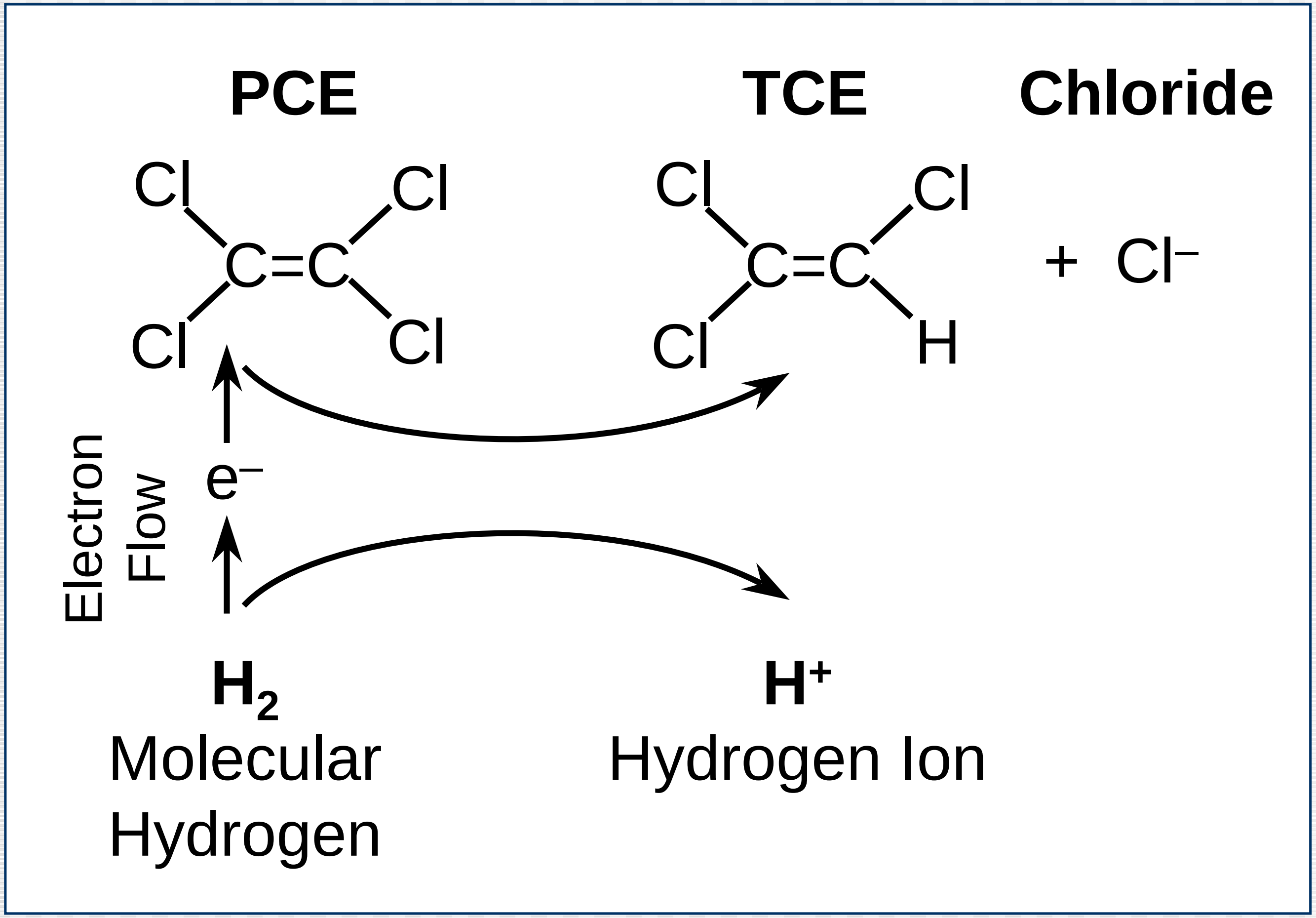
Steady-State Hydrogen Concentrations Reflect Redox Processes

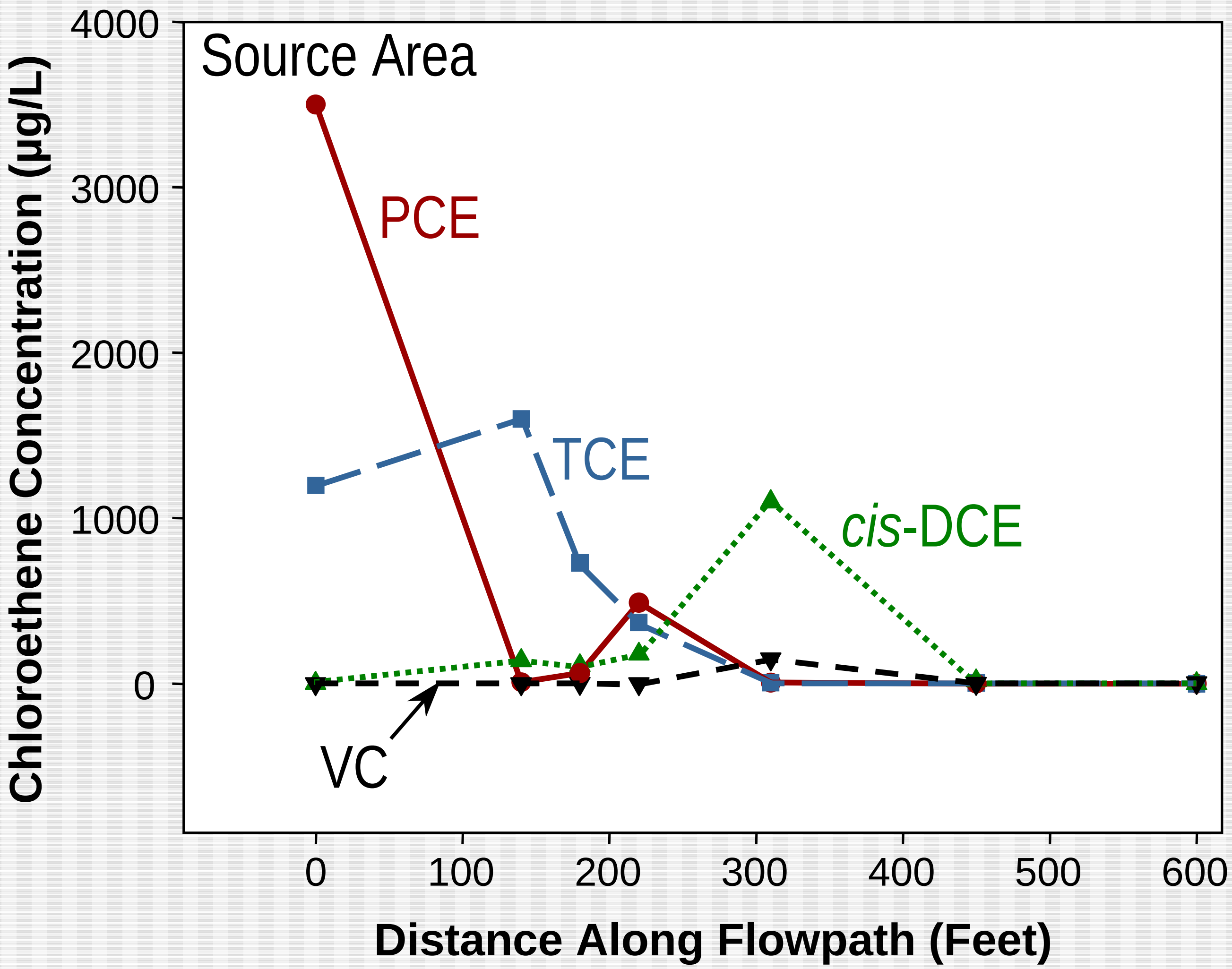
Terminal Electron-Accepting Process	Characteristic Hydrogen Concentration (nM)
Denitrification	0.1
Fe(III) Reduction	0.2 – 0.8
Sulfate Reduction	1.0 – 4.0
Methanogenesis	>5.0

Molecular Hydrogen (H_2) Drives Reductive Dechlorination



Source: Gosset and Zinder, 1996

Concentrations of Stages of Chlorinated Ethenes



So it Becomes Very Important to:

- Distinguish Oxidizing from Reducing Environments
- In Reducing Environments, to distinguish between:
  - Methanogenesis
  - Sulfate reduction
  - Fe(III) reduction
  - Nitrate reduction

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      - Laboratory Methods
        - Contaminant Loss
        - Radiotracer
        - Bioavailable Iron Assay
      - Field Methods
- Prediction/Verification
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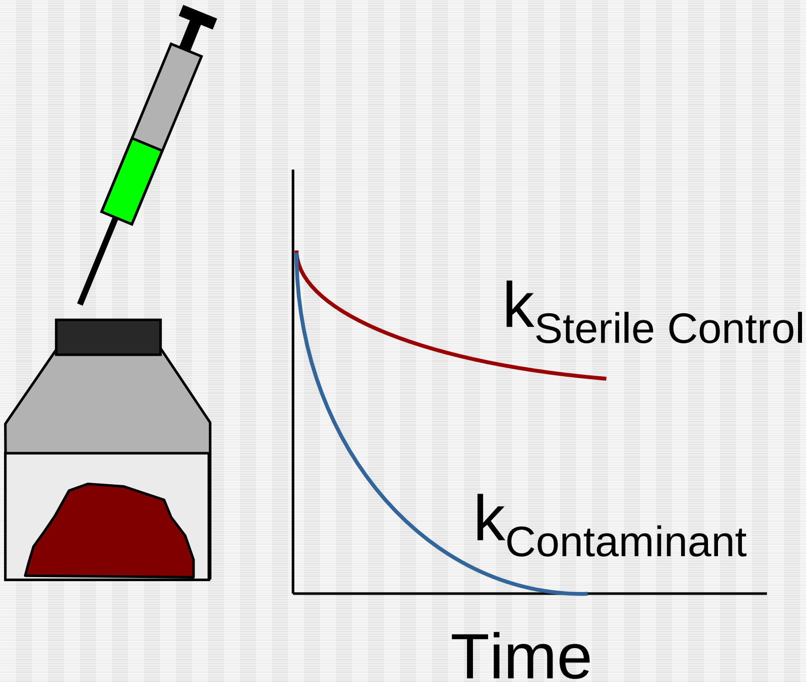
Development of a DH Analyzer and a Bioavailable Ferric Iron Assay

PROJECT NUMBER 200009
Carmen A. Lebron/NFESC
Dr. Patrick Evans/Camp Dresser & McKee Inc.

Goals:

- Demonstrate correlation between bubble strip method and DH analyzer
- Validate the bioavailable Fe(III) assay using
  - Redox characterization
  - Precipitants mineral characterization
  - Assessment of site data
- Quantify costs of each technology

Contaminant Loss Over Time, Microcosm Study



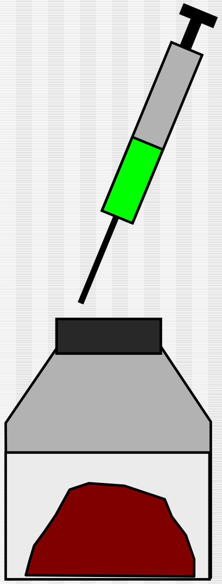
$$k_{bio} = k_{Contaminant} - k_{Sterile\ Control}$$

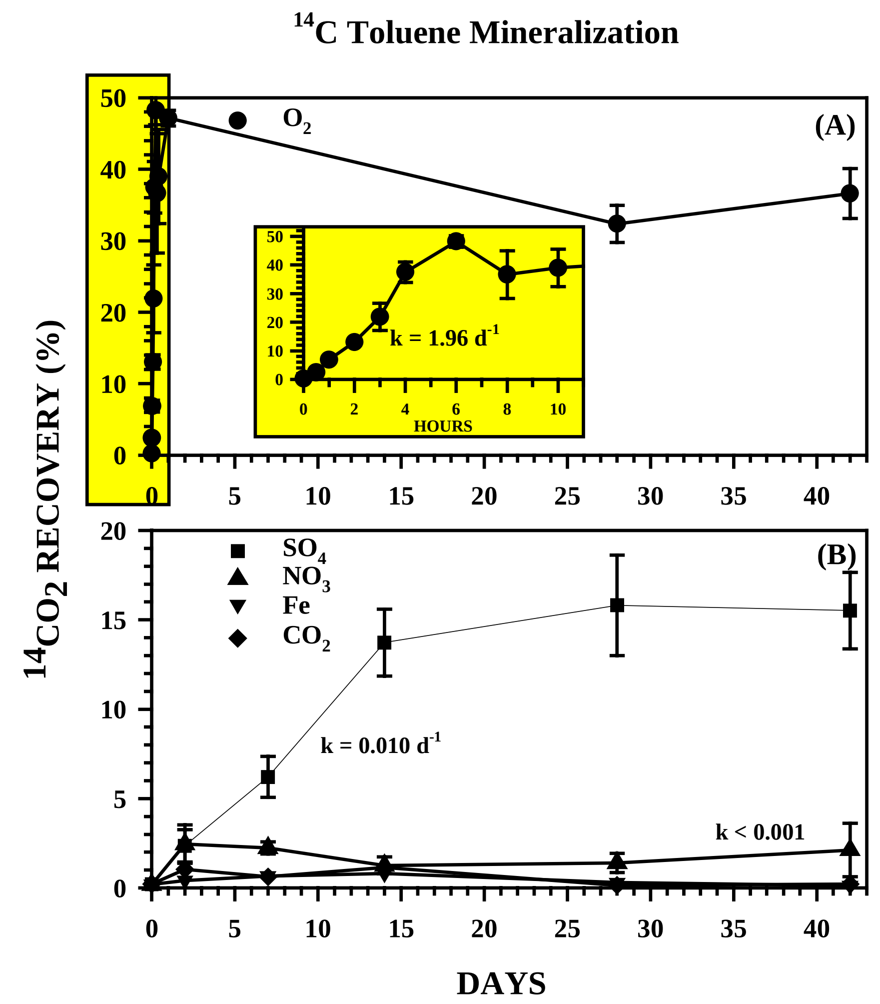
Limitations of Contaminant-Loss Approach:

- Often have to go on for long periods of time (up to a year), and in that time, the microbiology of the microcosm can change
- Are very expensive to do
- Results depend heavily on the skill of the investigator

Radiotracer Approach

- ^{14}C-Benzene → $^{14}CO_2$



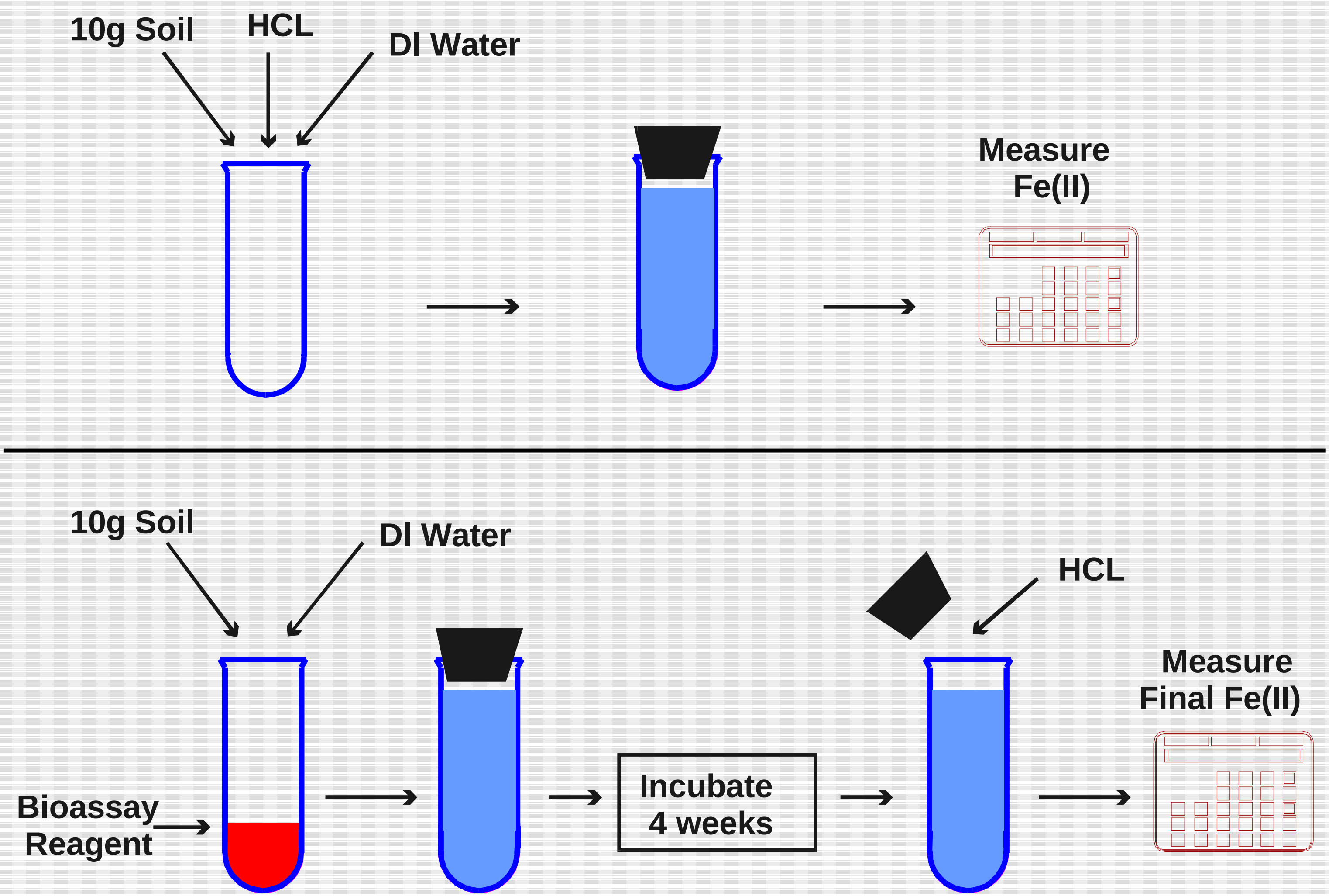


Limitations of Radiotracer Approach

- Results depend upon accurate matching of experimental to ambient electron-accepting conditions
- Results depend on skill of investigator

Bioavailable Ferric Iron Assay

Bioavailable Fe(III) Assay Protocol



Cost Comparison: Bioavailable Fe(III) Analysis

Method	Microcosm Research (Standard Assay Not Avail.)	Bioavailable Fe(III) Assay
Capital Cost	$0 if laboratory is available	$100
Cost/sample	$1,000 (assuming 10 samples)	$ 50
Implications	• Requires treatability laboratory • Requires specialized training • HCl extraction unacceptable	• Field kit • Like Hach kit

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- Redox
  - Equilibrium Approach
  - Kinetic Approach
- Hydrogen
- Bubble Stripping
- Hydrogen Analyzer
- Dispersion Model
- Conservative Tracer Model
- Flux Model

Methods for Evaluating Redox Processes in GW Systems

Equilibrium Approach:

- Based on Thermodynamic Equilibrium
  - Eh Measurements

Kinetic Approach:

- Based on Microbial Physiology
  - Identify Predominant Microbial Electron-Accepting Processes
  - Hydrogen Measurements

Equilibrium Approach (becoming out of date)

- Platinum Electrode Eh Measurements
- Measure Concentrations of Redox Couples
- > 0 = "oxidizing"
- < 0 = "reducing"

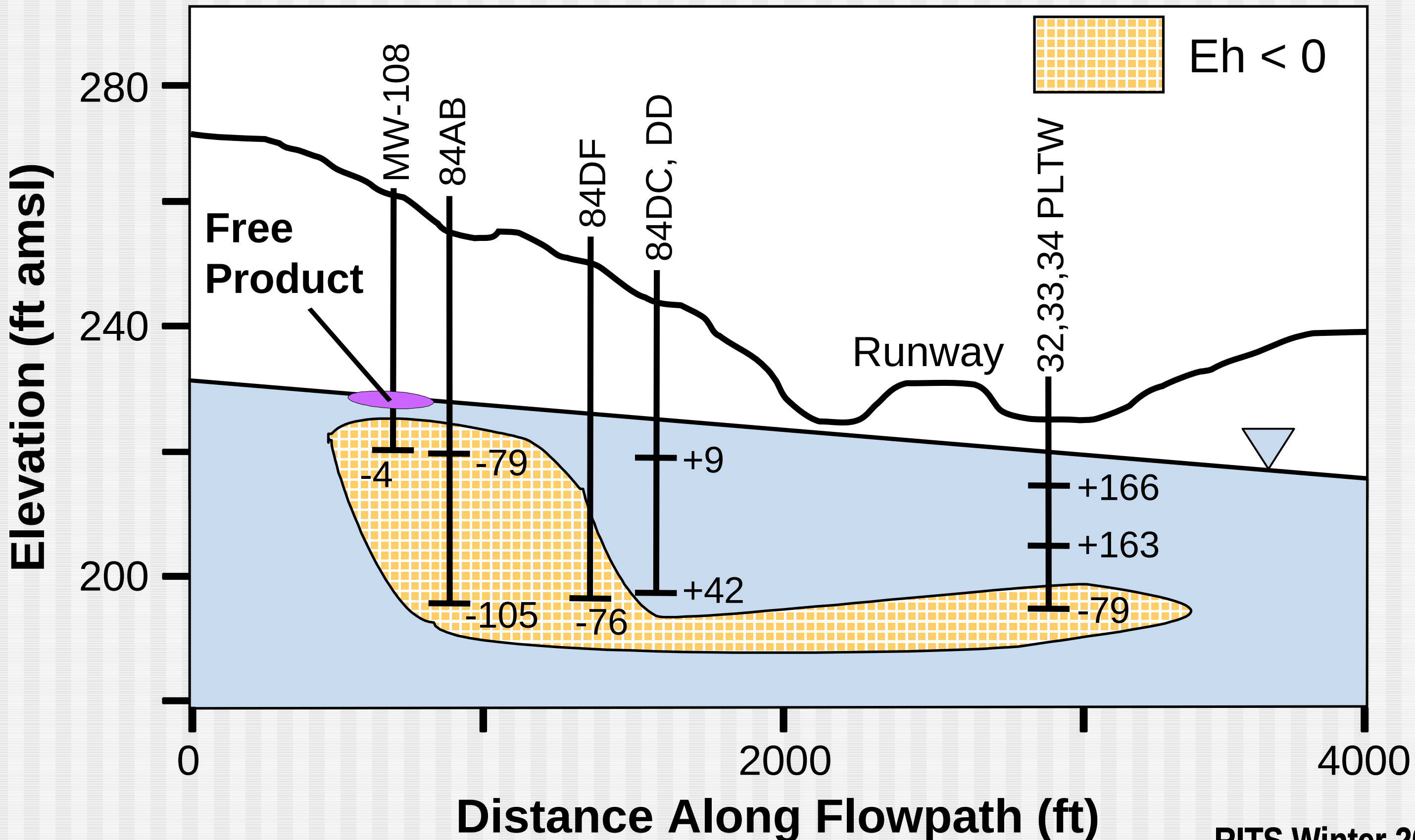
Kinetic Approach (more generally useful)

- Measure Concentration Changes of Electron Acceptors
- Measure Concentration Changes of Final Products
- Measure Concentrations of Transient Intermediate Products (Hydrogen)

Identifying Redox Processes

Plattsburg AFB: Eh

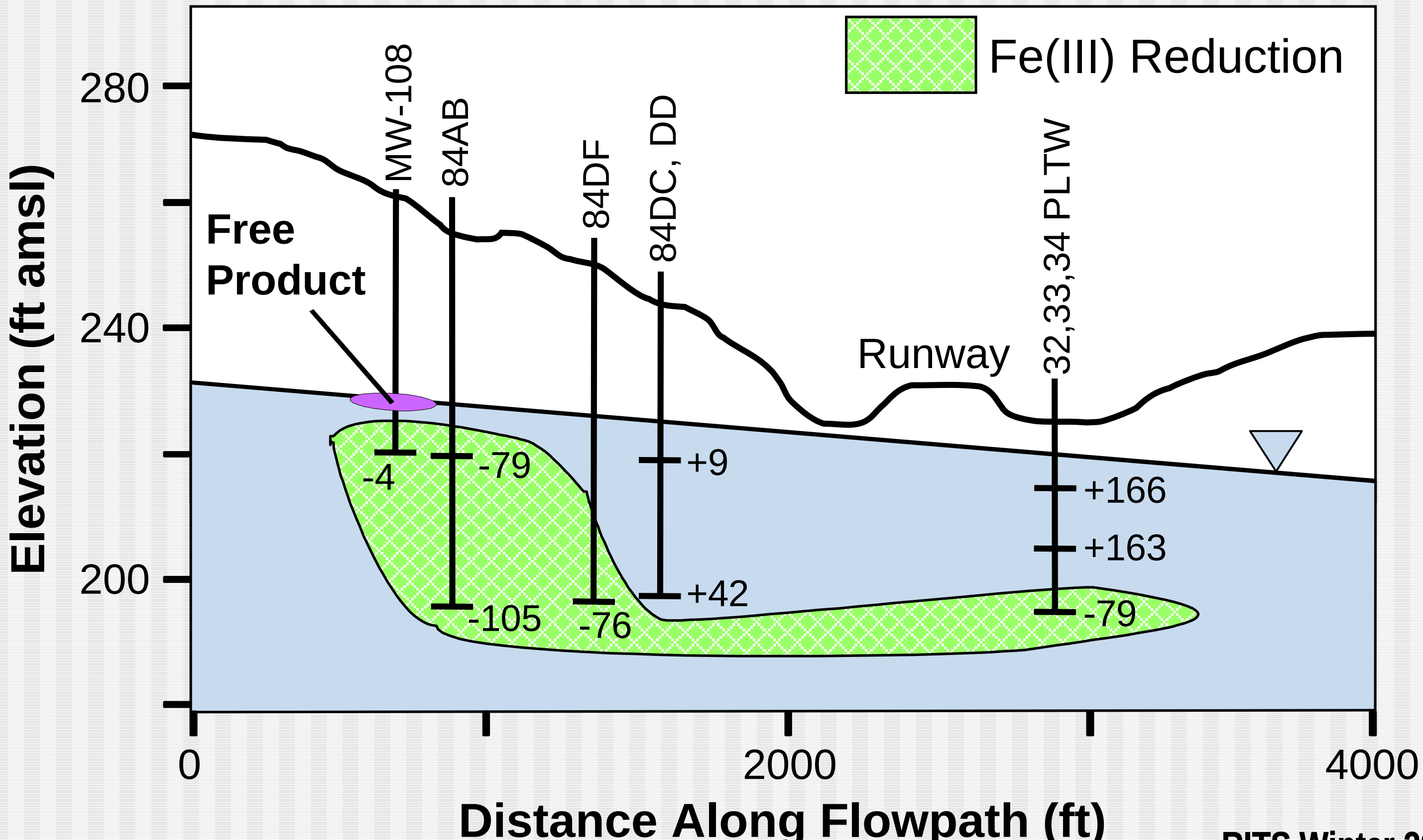
- Using: Equilibrium Approach



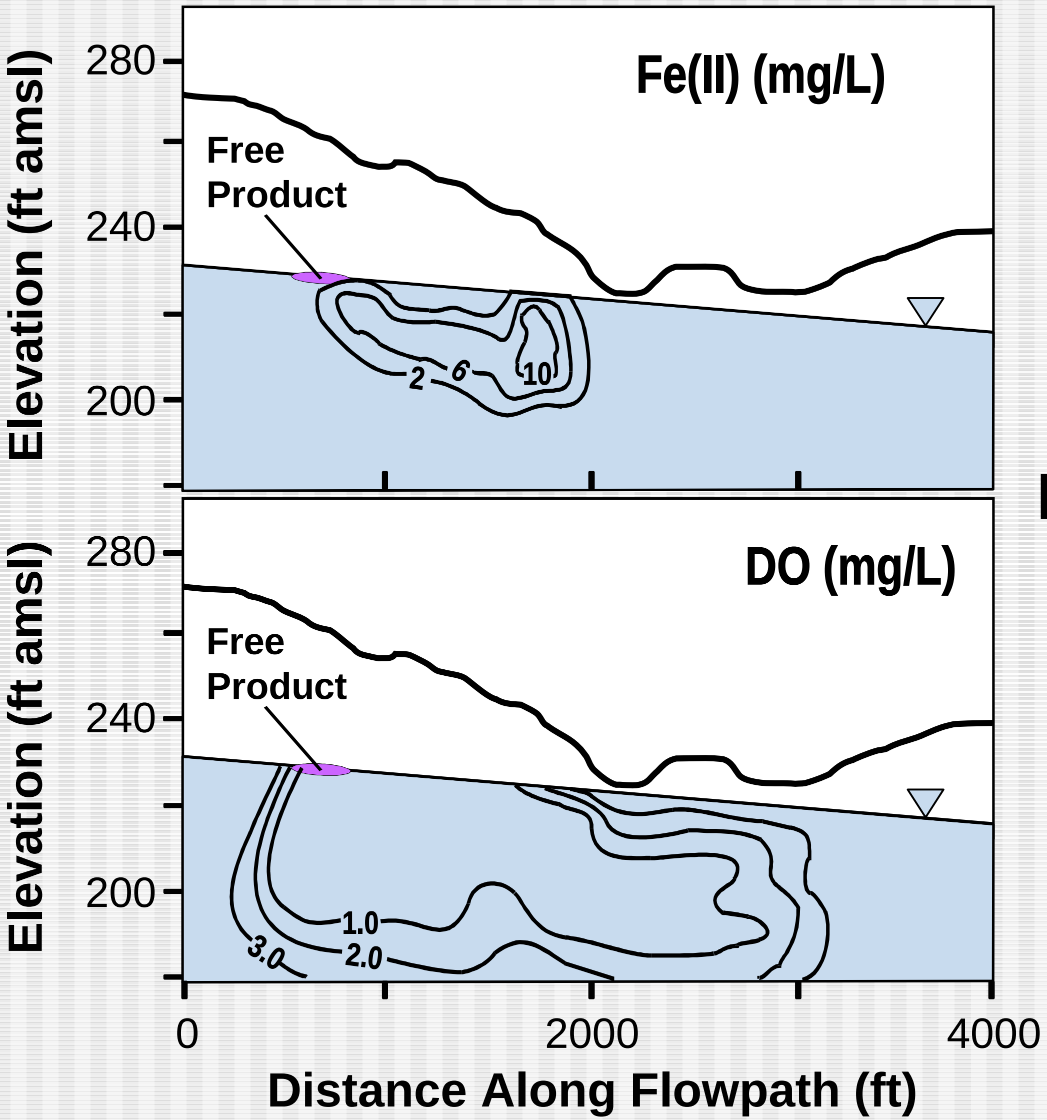
Equilibrium Approach Indicates that Fe(III) Reduction Predominates:

Plattsburg AFB

- Poor efficiency for Reductive Dechlorination
- Good efficiency for VC oxidation



Identifying Redox Processes



Plattsburg AFB

- Using: Kinetic Approach

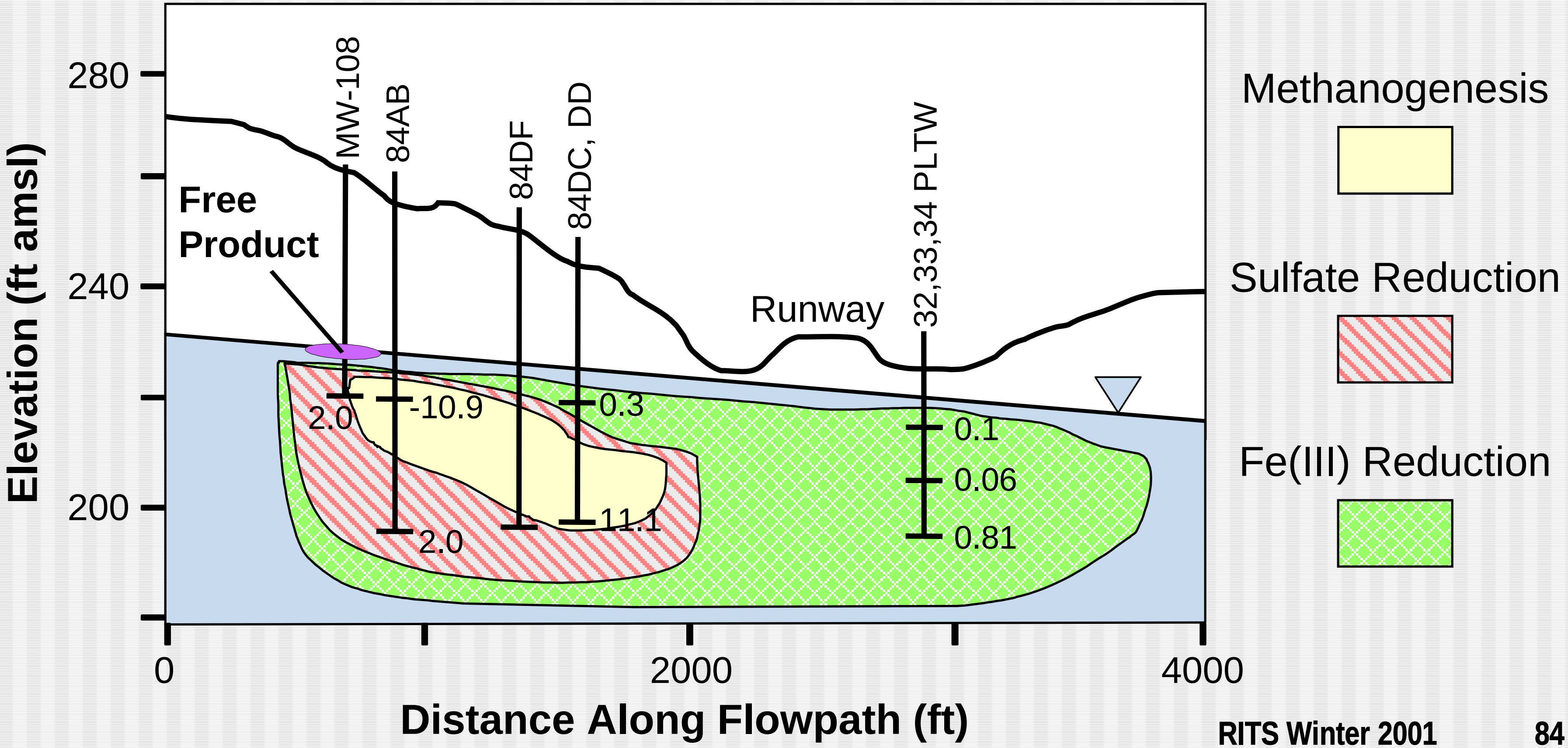
Fe(II) and DO Concentrations

Identifying Redox Processes

Plattsburg AFB

- Using: Kinetic Approach

DH (H_2) Concentrations

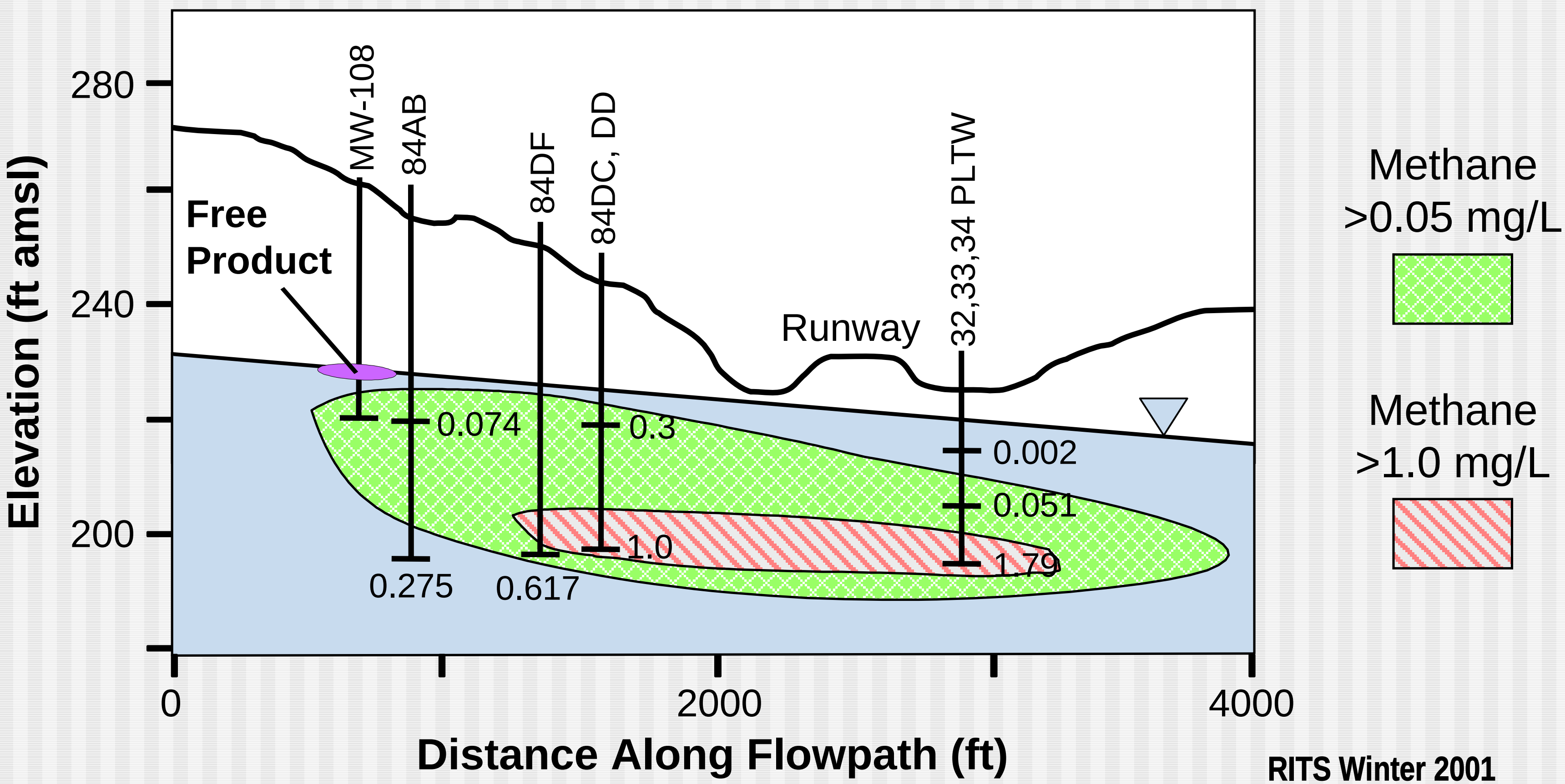


Identifying Redox Processes

Plattsburg AFB

- Using: Kinetic Approach

Methane Concentrations

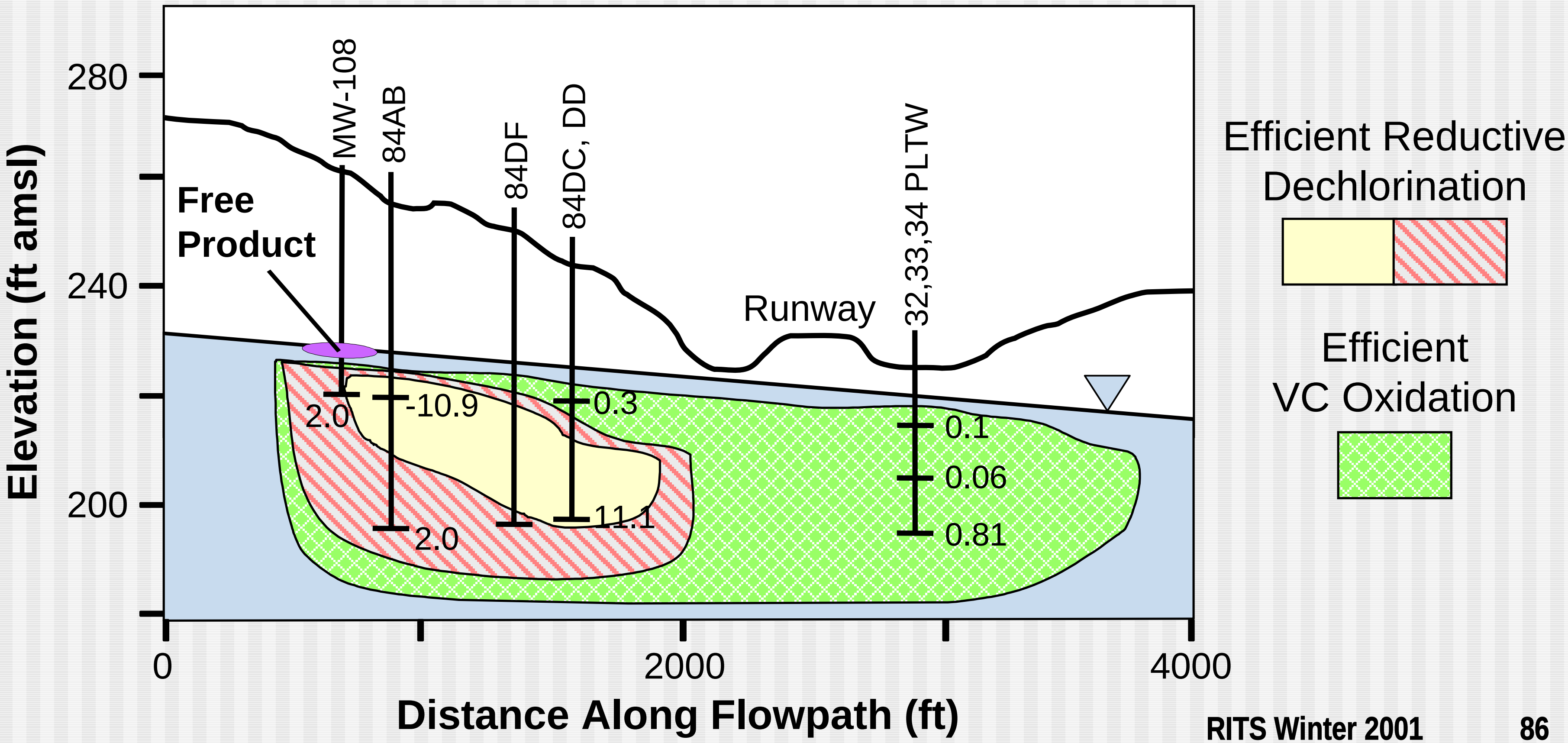


Identifying Redox Processes

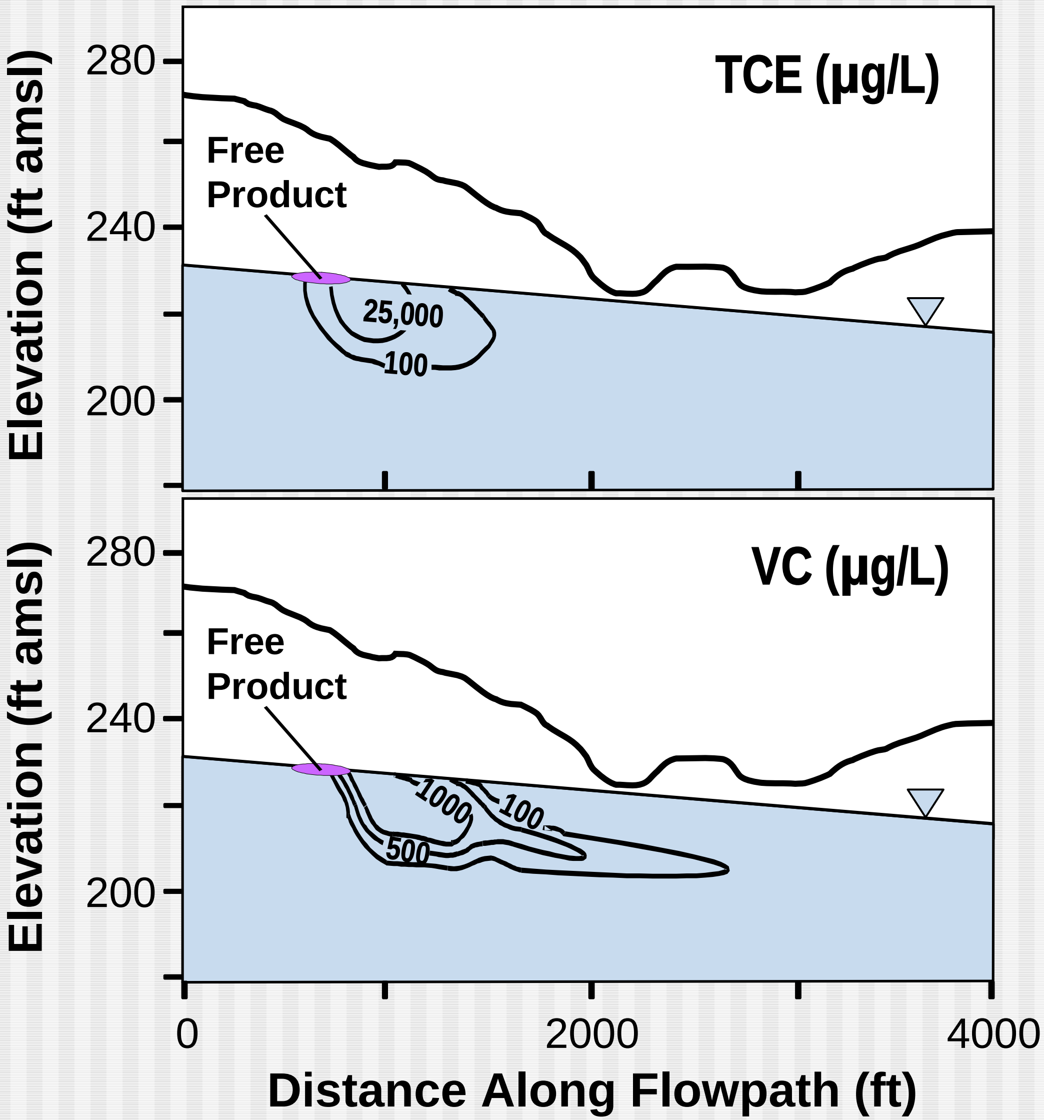
Plattsburg AFB

- Using: Kinetic Approach

Redox Zonation and Predicted Contaminant Fate



Identifying Redox Processes



Plattsburg AFB

- Using: Kinetic Approach

TCE and VC Concentrations

How Redox Conditions Affect NA at Plattsburgh AFB

- Methanogenic conditions at contaminant source produces DCE and VC
- Fe(III)-reducing conditions in plume oxidizes VC

Redox Conclusions

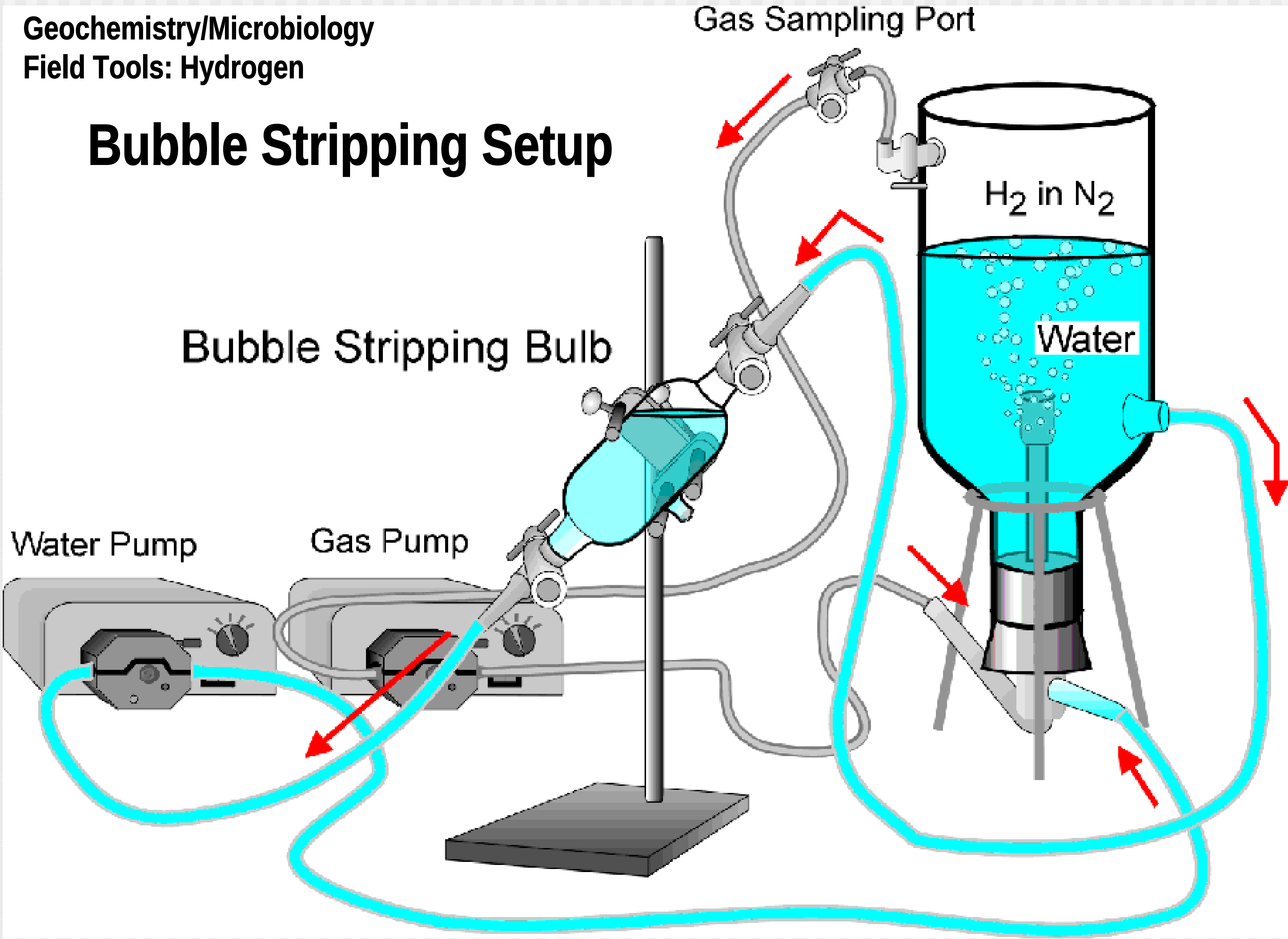
- The Equilibrium Approach did not accurately characterize the redox chemistry at this site
- The Kinetic Approach accurately identified discrete methanogenic, sulfate-reducing, and Fe(III)-reducing zones
- The sequential methanogenic-Fe(III)-reducing conditions lead to efficient natural attenuation

When Hydrogen Analyses are Useful

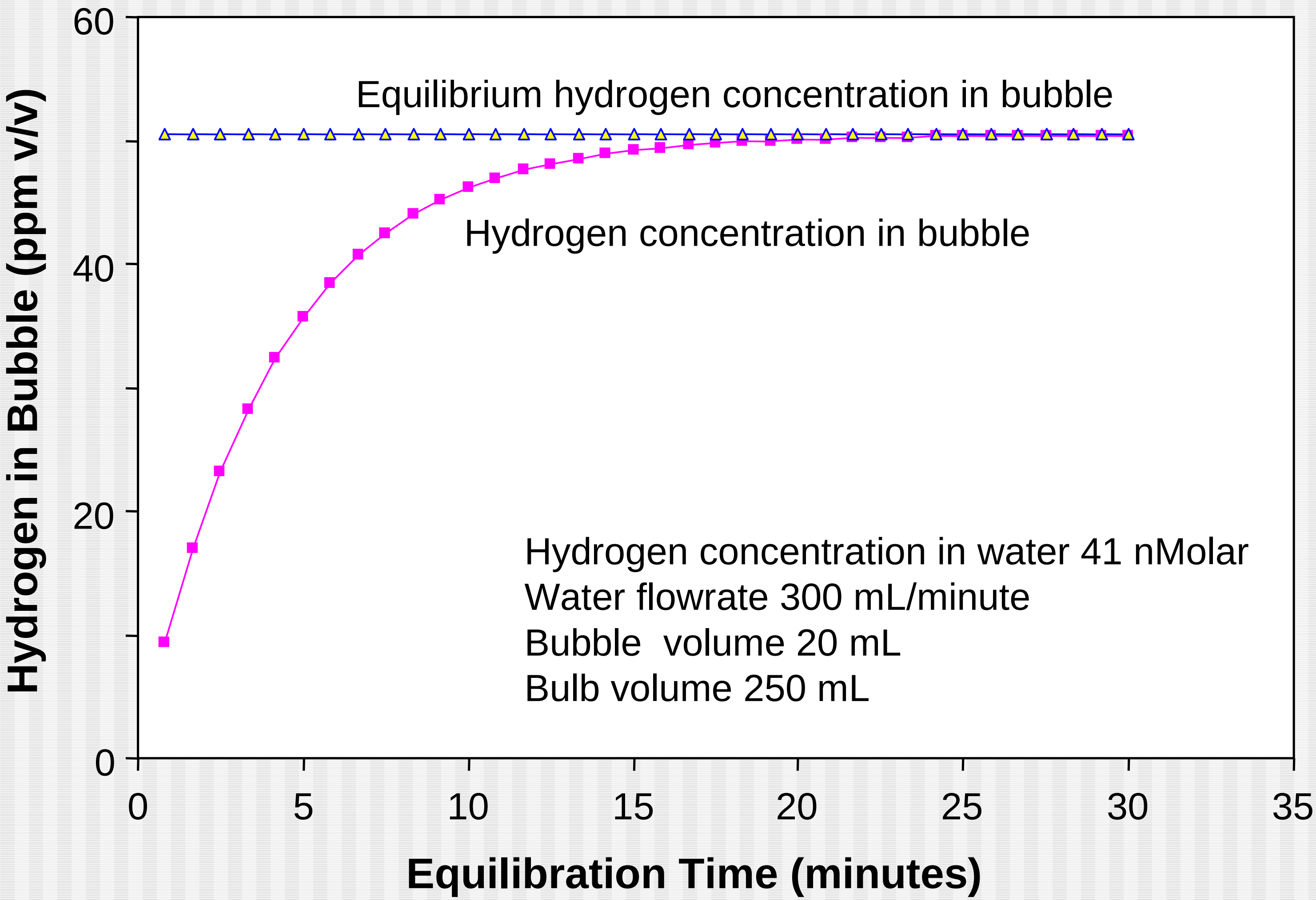
- Already showed example of hydrogen at Laurel Bay, but usefulness at PH-contaminated site is limited
- Some chlorinated solvents plumes are being attenuated without the appearance of transformation products
- Some indicators are mobile!

Geochemistry/Microbiology
Field Tools: Hydrogen

Bubble Stripping Setup



Bubble Stripping Results

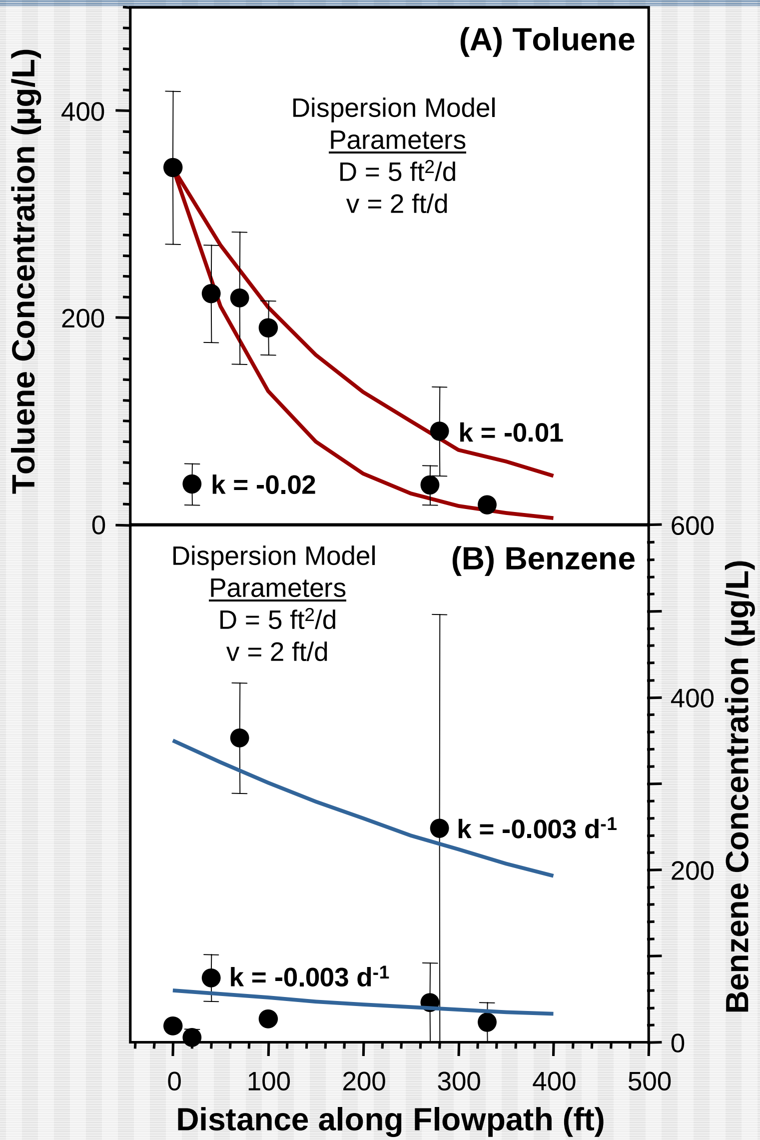


Dissolved Hydrogen Analyzer

Cost Comparison: DH Analysis

Method	On-Site Bubble Strip with Reduction Gas Analyzer	DH Analyzer
Capital Cost	$30,000 (Trace RGA)	$5,000
Cost/sample	$100 (Microseeps fee)	$20
Implications	• Requires specialized training • Faulty sampling methodology can yield misinterpretation of data • Option is to sample and send gas to fixed lab • Off-site analysis does not allow for QA/QC of sampling method	• Makes sampling independent of user • Field analysis

Dispersion Model Approach

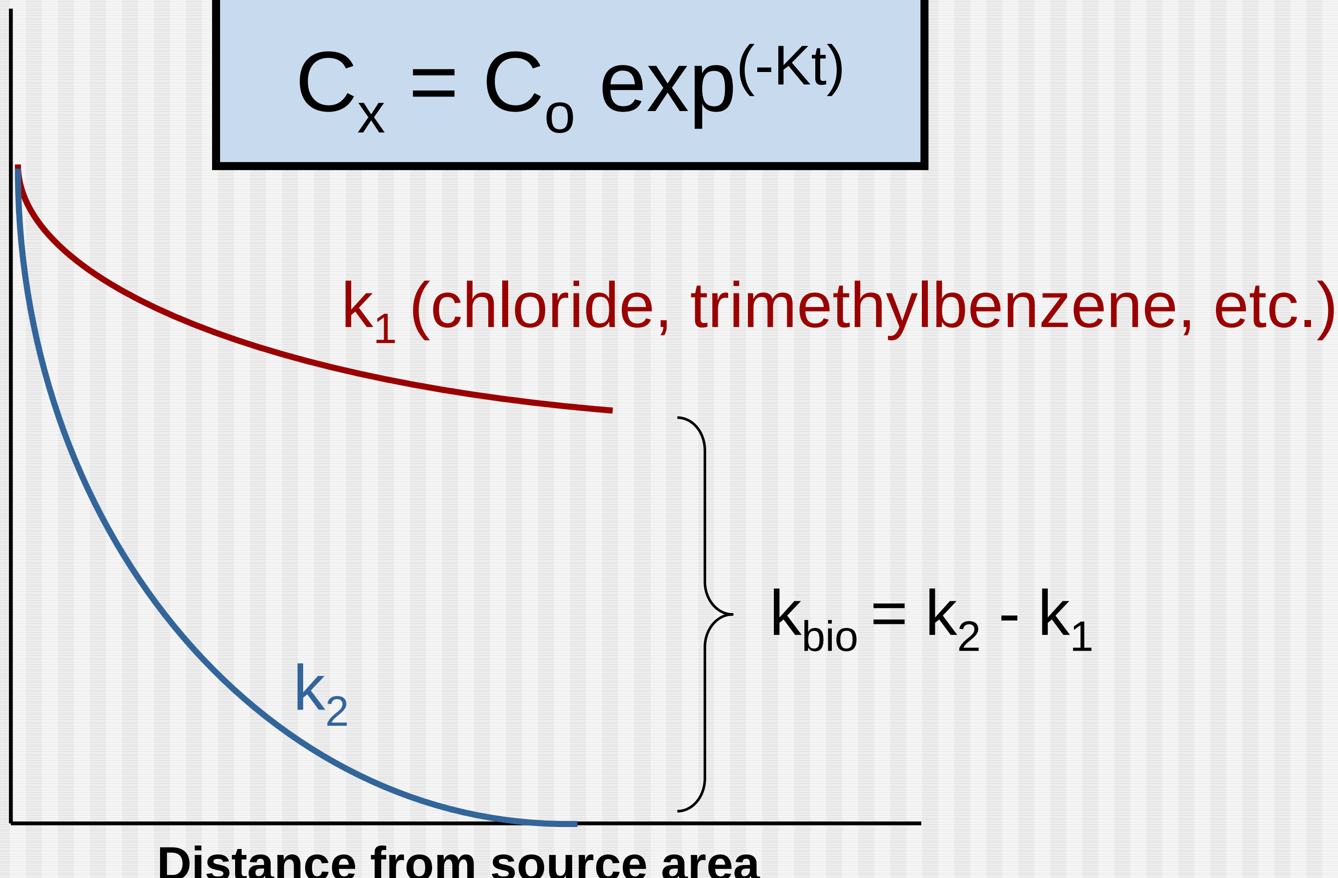


- Assumes D and v are known, so that k can be determined by curve-fitting

Conservative Tracer Approach

- Compares degrading vs. nondegrading solutes:

$$C_x = C_o \exp^{(-Kt)}$$



How do these Field vs. Lab Methods Compare?

Clearly, any biodegradation rate measurements are order-of-magnitude estimates, because:

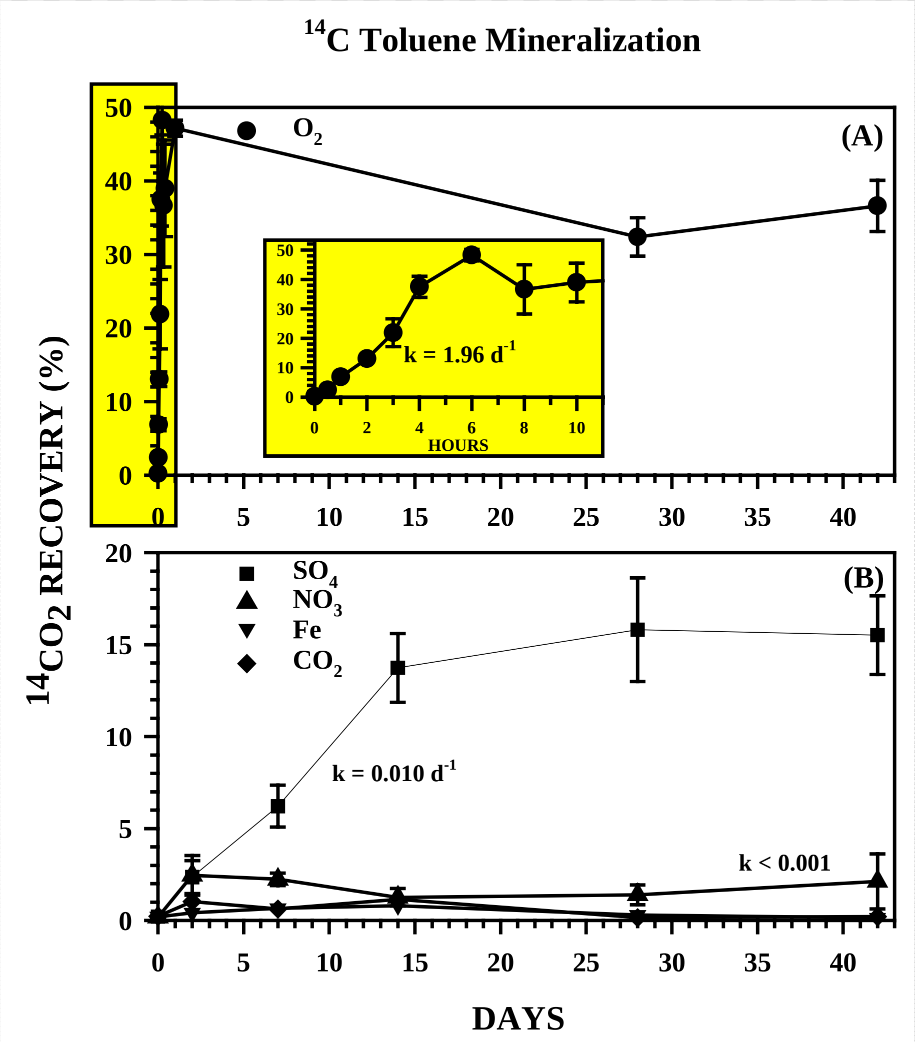
Field methods

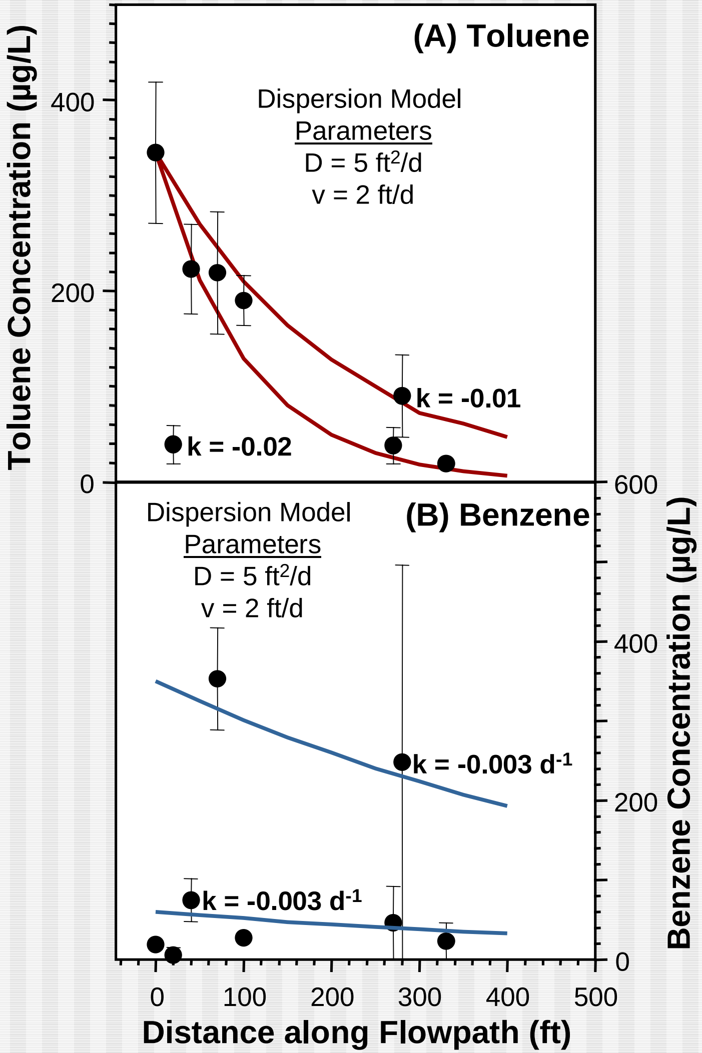
- Poor characterization of the plume
- Hydrologic variability

Laboratory methods

- Investigator-skill bias
- Improper matching of field to lab conditions

Radiotracer Approach vs. Dispersion Model





Potential Shortcomings of Both Models

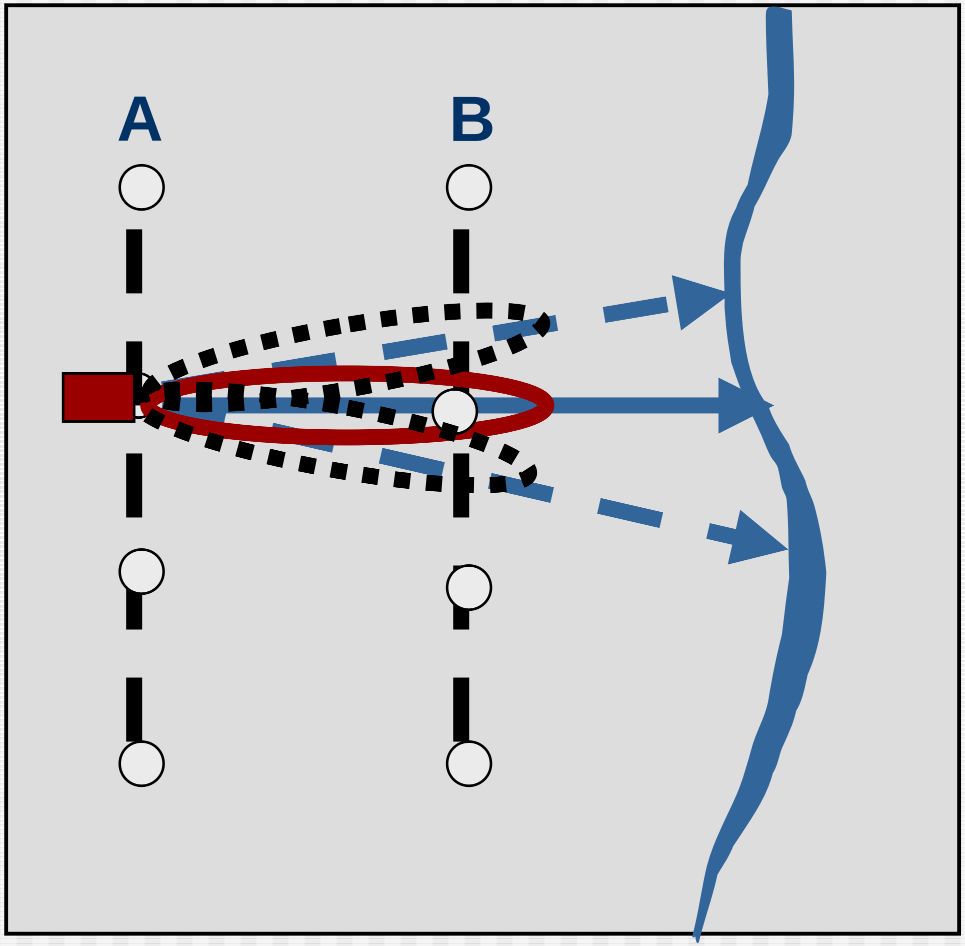
Radiotracer Approach vs. Dispersion Model

- Need to know GW flowpath
- GW wells need to be along that flowpath
- Flowpath needs to remain fixed in space and time
- Steady-state conditions
- Presence of conservative tracer

Possible alternative approach without these constraints:

Flux Model Approach

Shifting GW flowpaths shifts plume centerline



Flux approach is more realistic, b/c total mass would be included

Compute rate of mass flux for each cross section

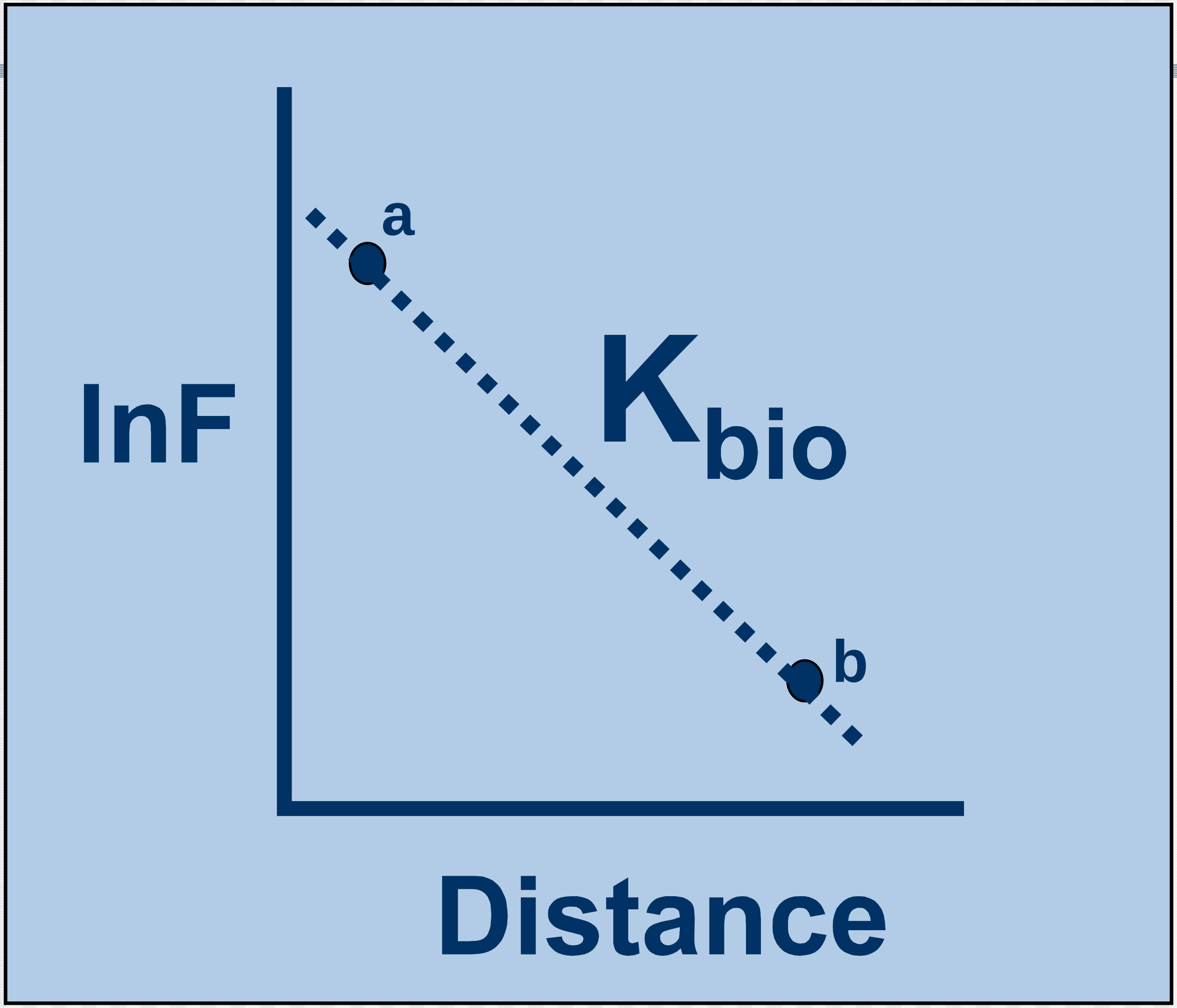
$$F = \sum_{i=1}^{n} (C*A*q)$$

$$F_x = F_o \exp^{(-Kt)}$$

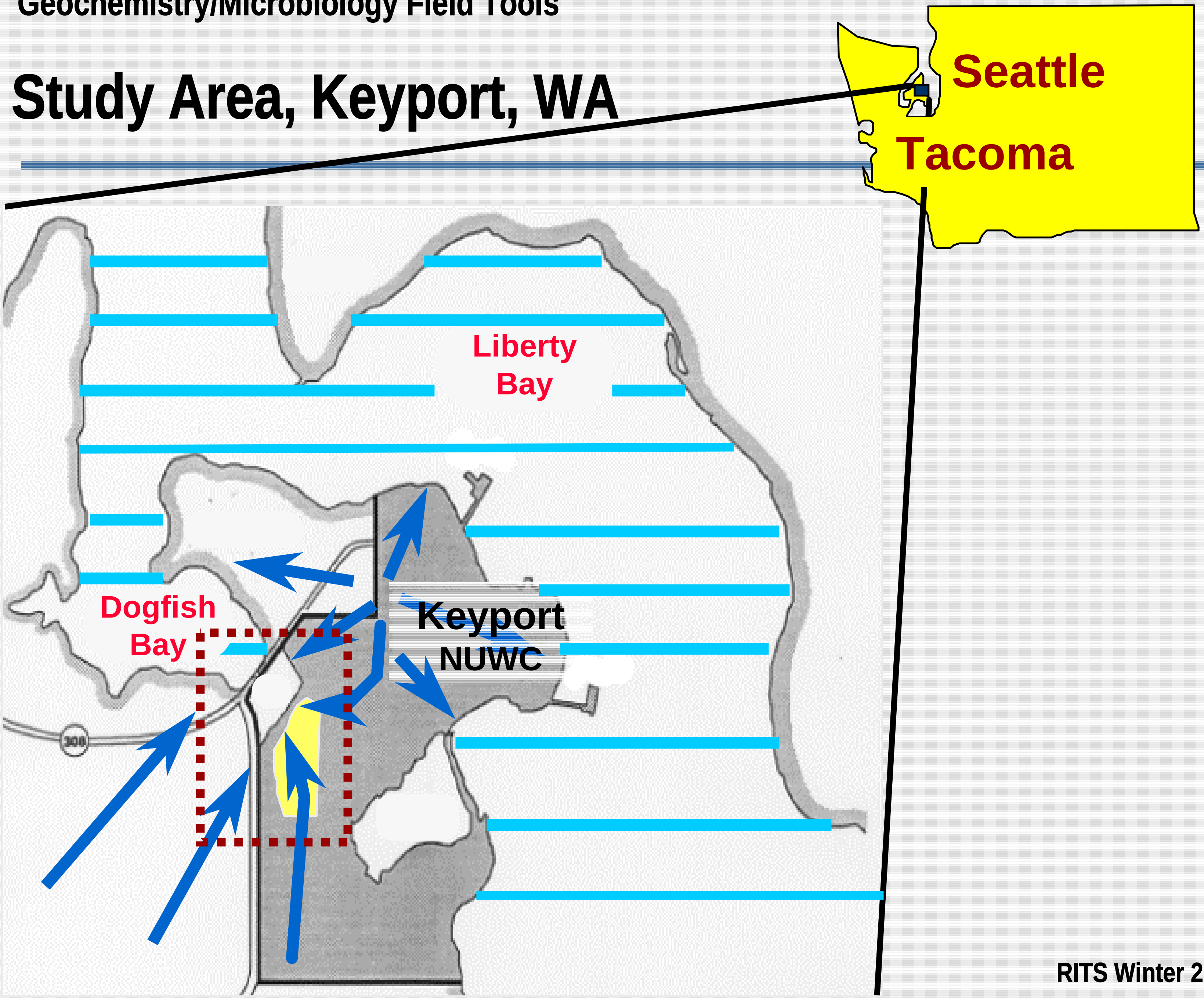
$$t = D/v$$

$$\ln F_b = \ln F_a - (K/v)D$$

(units of F are Mass per time, or microgram/day)


lnF
a
b
Kbio
Distance

Study Area, Keyport, WA

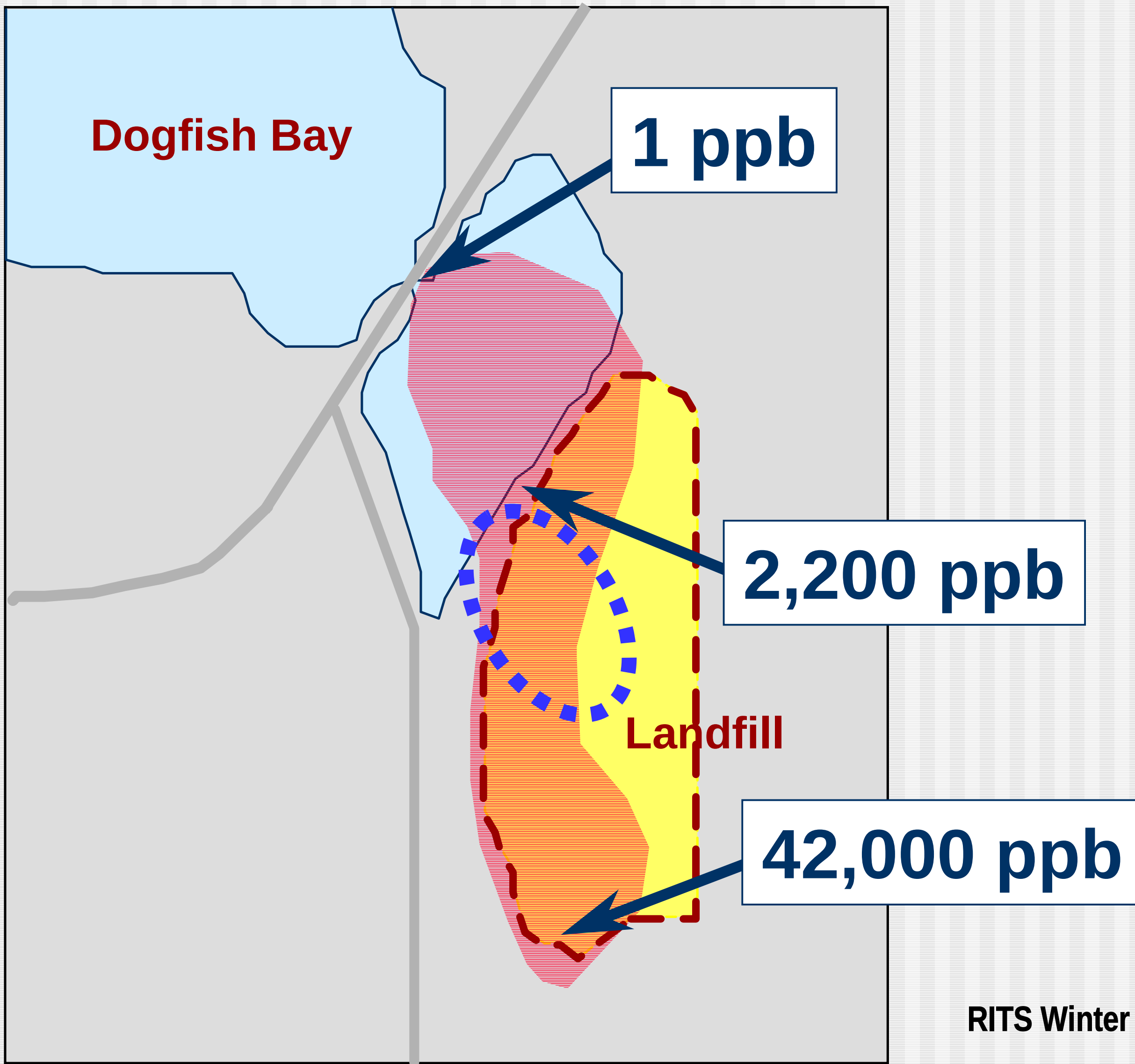


Chlorinated VOC Plume

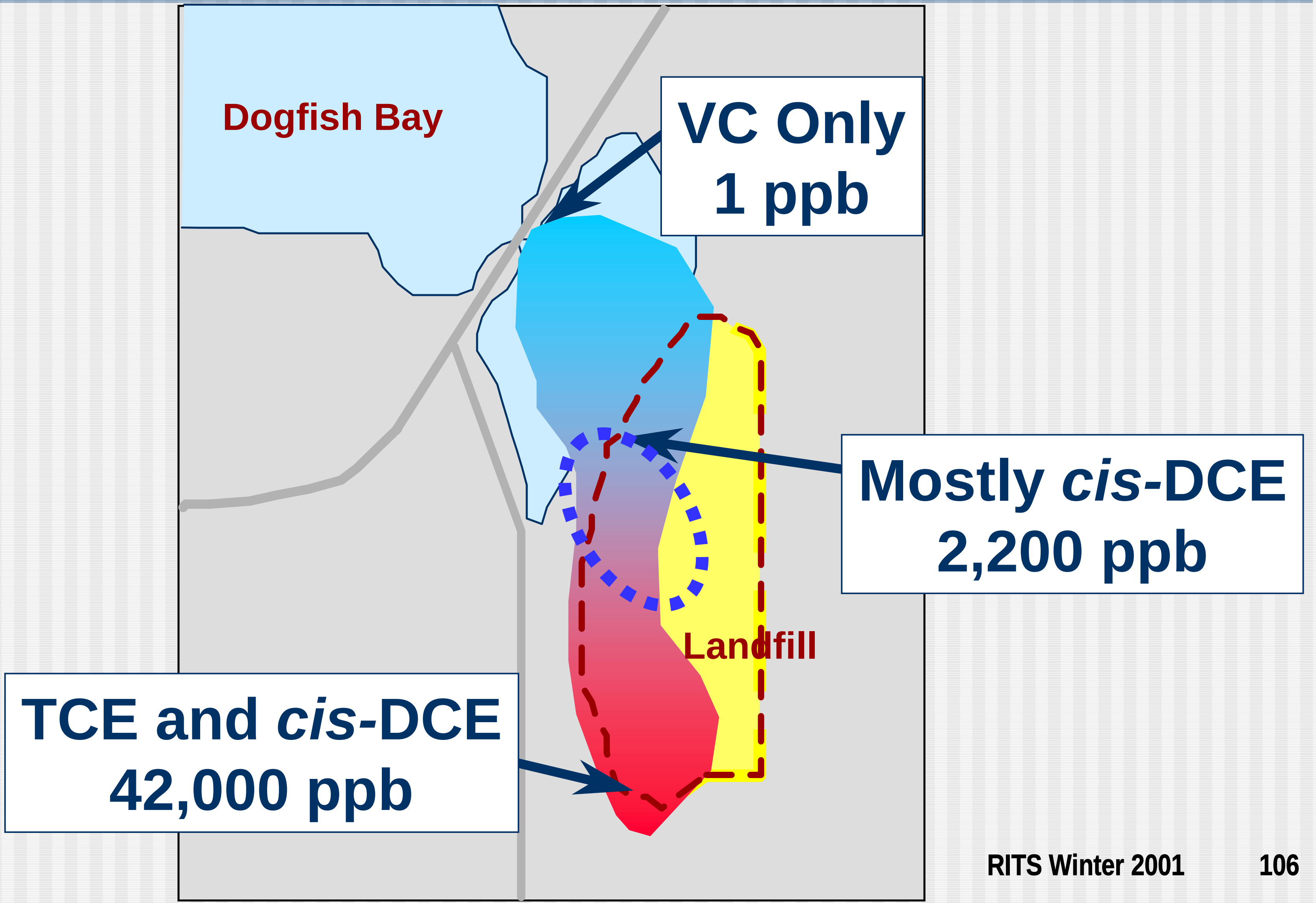
Sept. 1996

April 1997

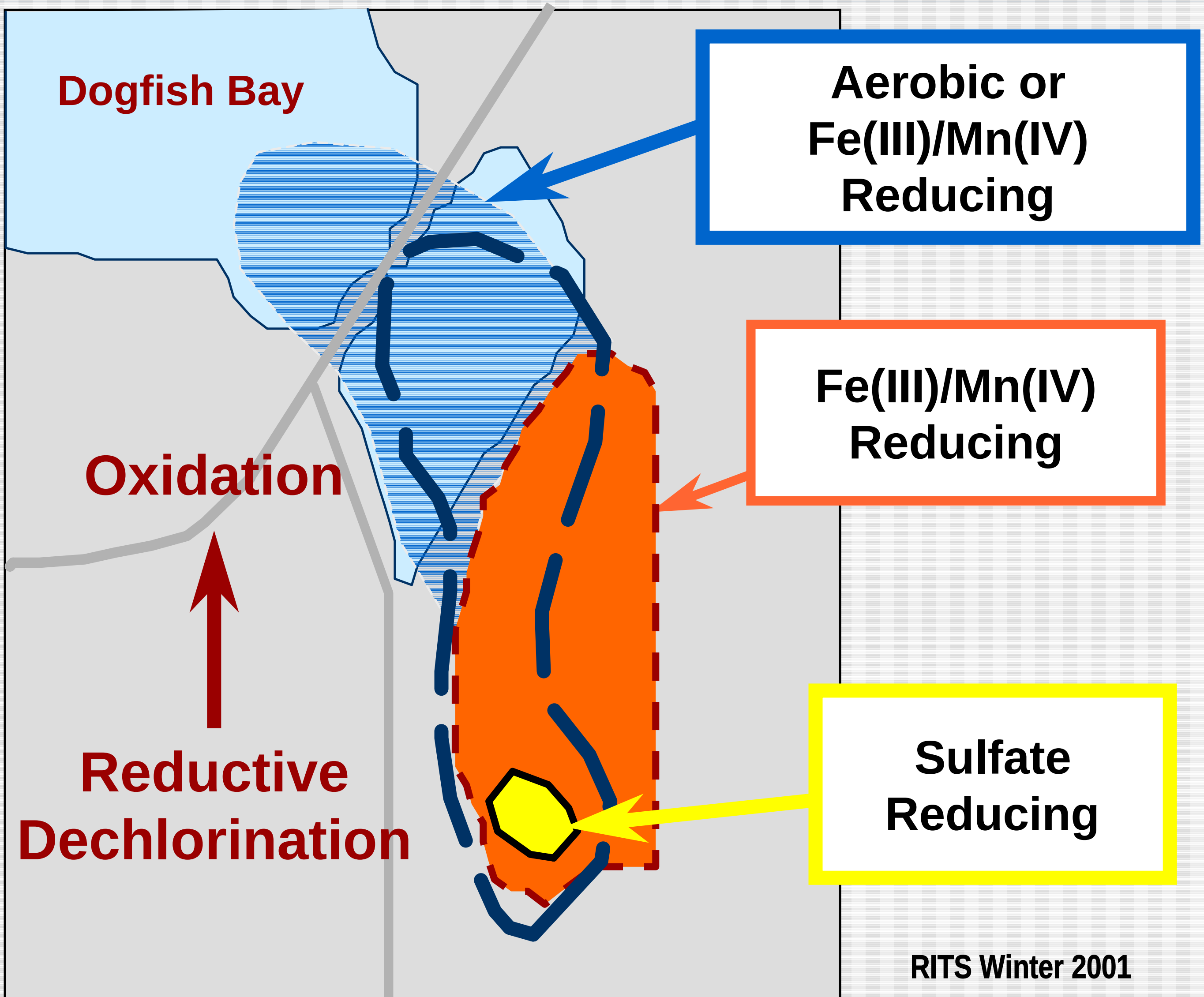
March 1998



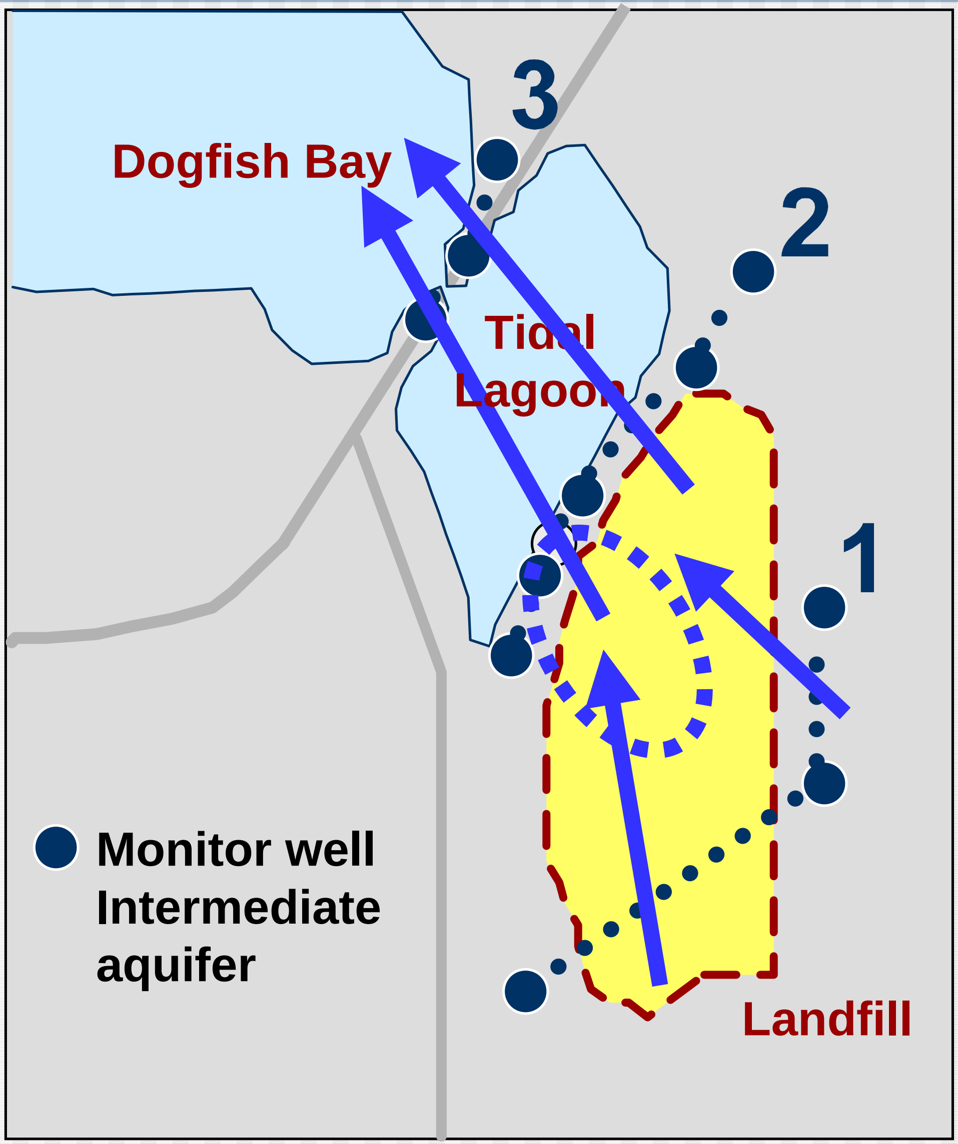
Field Evidence (VOCs) for Biodegradation



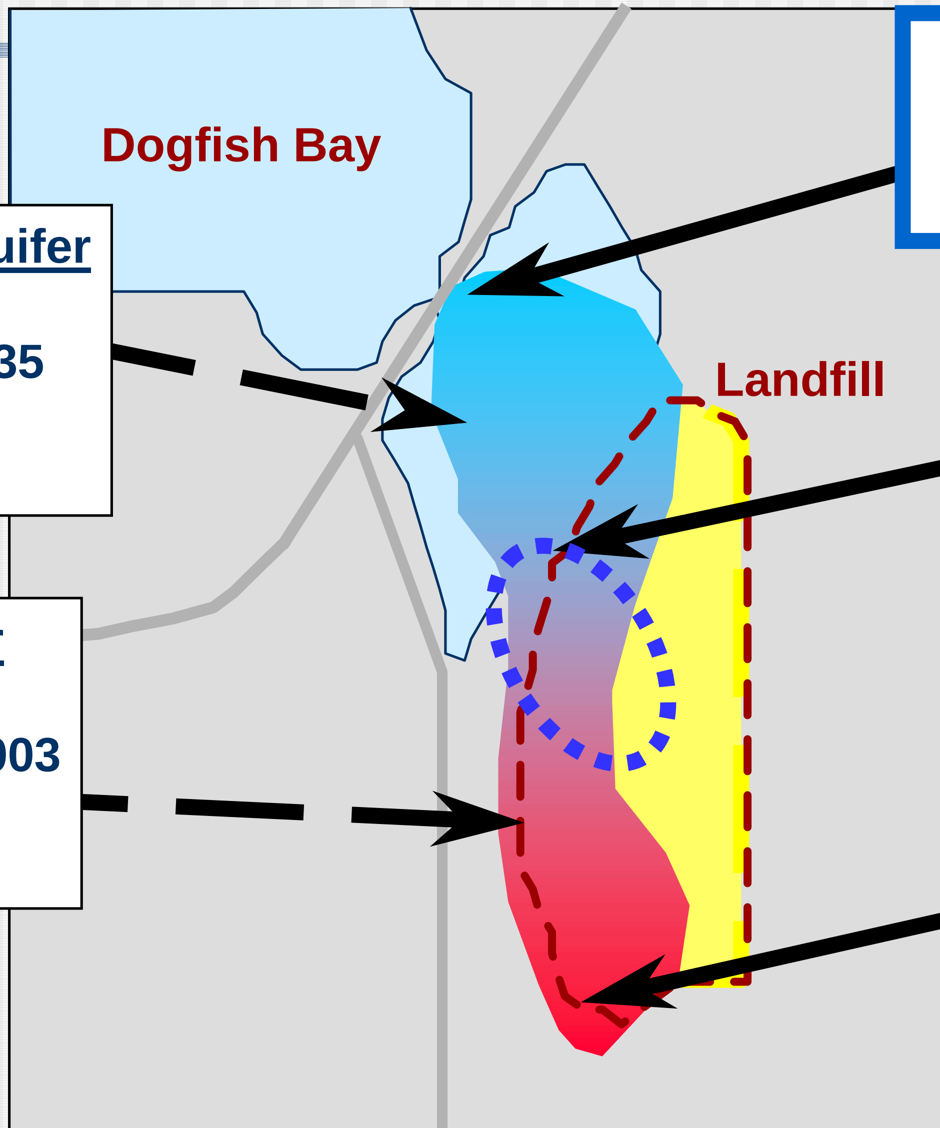
Distribution of Redox Processes



Intermediate Aquifer



September 1996 Biodegradation Rates (d-1)



Intermediate aquifer
VC = –0.003
cis-DCE = –0.0035
TCE = –0.002
PCE = none

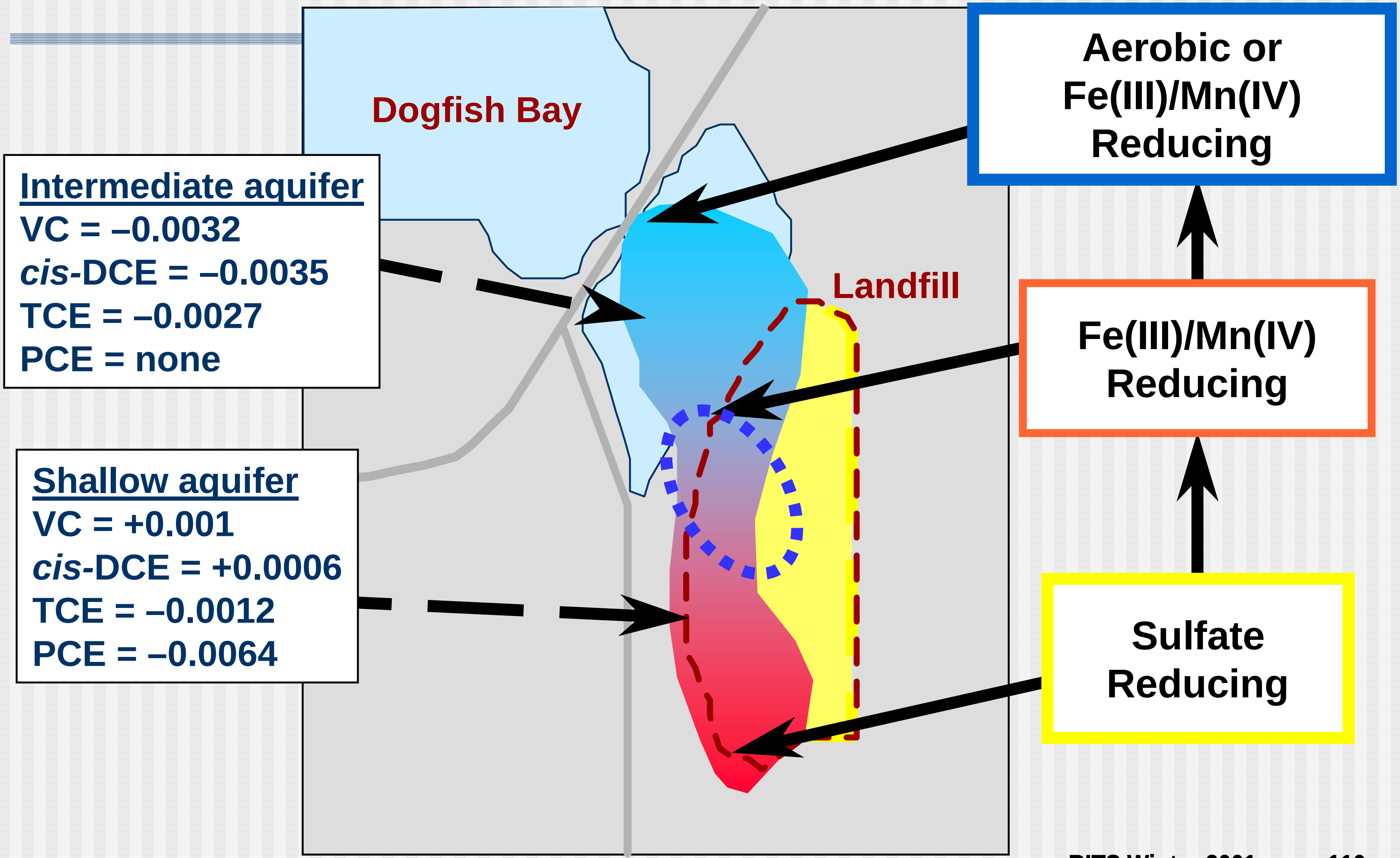
Shallow aquifer
VC = +0.000005
cis-DCE = –0.0003
TCE = –0.002
PCE = –0.006

Aerobic or Fe(III)/Mn(IV) Reducing

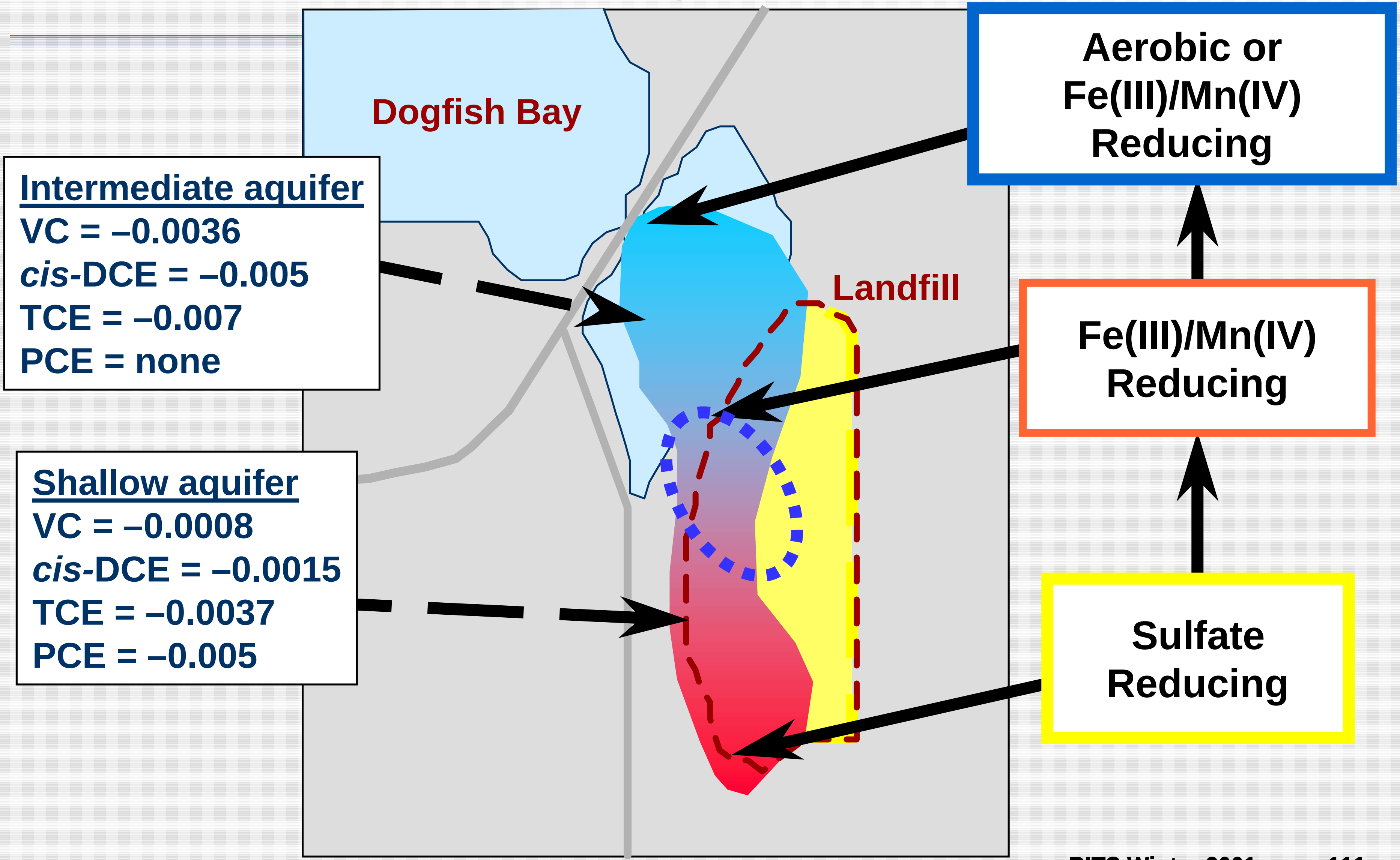
Fe(III)/Mn(IV) Reducing

Sulfate Reducing

April 1997 Biodegradation Rates (d^{-1})



March 1998 Biodegradation Rates (d^{-1})



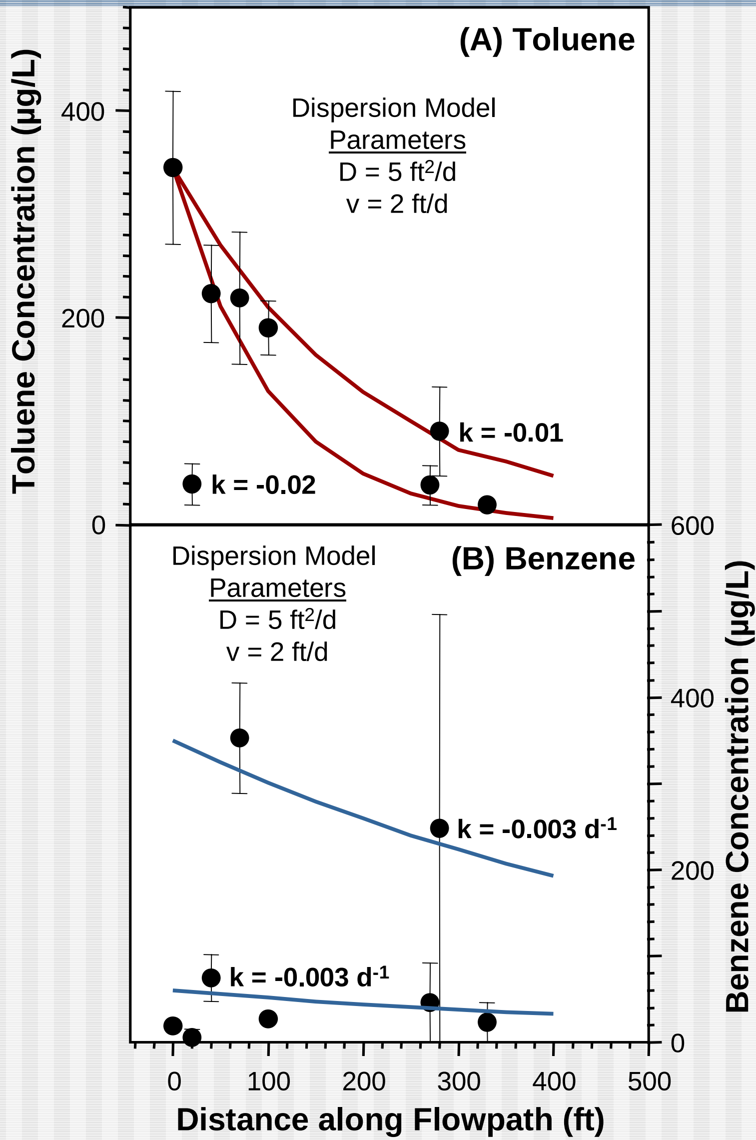
Half-Lives (ln2/bio. rate): Intermediate Aquifer

TCE	(ln2/-0.0041)	0.46 years
***cis*-DCE**	(ln2/-0.004)	0.47 years
***trans*-DCE**	(ln2/-0.0044)	0.43 years
1,1-DCE	(ln2/-0.0063)	0.30 years
VC	(ln2/-0.0032)	0.59 years

MNA Outline

- Background
- Assessment
- Prediction/Verification
  - "Natural Attenuation Capacity" Method
- References
- Points of Contact

Dispersion Model Approach



- Assumes D and v are known, so that k can be determined by curve-fitting

Numerical Solutions to GW Flow/ST Equation:

- BIOPLUME (1,2,3, Son of Bioplume, etc.)
- BIOSCREEN
- MODFLOW
- SUTRA
- MT3D
- Assimilative Capacity (MNA) Screening Tool Spreadsheet

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MNA References

- Chapelle, 1999, Ground Water, v. 37: 122-132.
- EPA OSWER Directive 9200.4-17P,1999. Use of Monitored Natural Attenuation at Superfund, RCRA, Corrective action, and UST sites.
- Chapelle, Landmeyer, and Bradley, 1996. USGS WRIR 95-4262.
- Landmeyer, Chapelle, and Bradley, 1996. USGS 96-4026.
- Chapelle, Robertson, Landmeyer, and Bradley, 2000. USGS WRIR 00-4161.
- Lovley, Chapelle, and Woodward, 1994. Environmental Science & Technology, v. 28: 1205-1210.
- Bradley and Chapelle, 1996. Environmental Science & Technology, v. 30: 2084-2086.
- Chapelle and others, 1997. Environmental Science & Technology, v. 31: 2873-2877.
- Landmeyer and others, 1998. Ground-Water Monitoring and Remediation, v. 18: 93-102.

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MNA Points of Contact

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